

Theoretical Investigation of Co Nanoparticles Structures and Mn Promotion for the Fischer-Tropsch Synthesis

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Abstract

The Fischer–Tropsch (FT) synthesis occupies a central position among the possible routes to produce Sustainable Aviation Fuels (SAFs) due to its feedstock flexibility and its ability to produce long-chain hydrocarbons. Cobalt-based catalysts are the industrial benchmark for low-temperature FT synthesis, offering high activity, stability, and selectivity toward C_{5+} products. However, catalyst deactivation, structural sensitivity, and incomplete mechanistic understanding of promoter effects continue to limit further performance improvements. In particular, manganese promotion has emerged as an effective strategy to enhance C_{5+} selectivity, yet its underlying mechanistic and structural role remains insufficiently understood.

This thesis presents a comprehensive theoretical investigation of pristine and Mn-promoted Co catalysts for FT synthesis, with a primary focus on structural modeling. It is postulated that a top-down approach where catalytic insights are derived from structural features may provide broader insights than conventional mechanistic modeling, as many of the unresolved aspects regarding FT Co catalysts transcend purely nanoscale electronic effects.

The first part of the work establishes a DFT-based Monte Carlo (MC) framework to model cobalt nanoparticles (NPs) as a function of particle size and metal–support interactions (MSI). This approach relies on a DFT-derived energy model employed in a MC algorithm, that in turn distributes metal atoms in a fixed fcc 3D grid searching for low-energy structures. The energy model assumes linear scaling of the energy of Co atoms with their coordination number (CN) and is validated against DFT calculations. The simulations reveal a systematic increase in the concentration of undercoordinated step and kink sites with particle size in the investigated range, in line with the experimentally observed structure sensitivity of cobalt FT catalysts. Increasing MSI lead to flattening of the NPs but hardly affect the site distributions. An extensive classification of the different fcc low-coordinated sites (LCS) is further established, which shows that while edges and corners dominate the small particles, steps and kinks become predominant with increasing size. Direct CO dissociation calculations reveal the existence of particularly active LCS that had been historically overlooked.

CN-specific energy corrections accounting for CO adsorption are subsequently incorporated in the energy model. CO is found to induce pronounced surface reconstruction, characterized by an increase in B5-A step sites at the expense of (111) and (100) terraces. In addition, CO adsorption substantially lowers the NPs surface energies, thereby markedly modifying the Co NPs stability profiles. Ostwald ripening simulations reveal a dramatic acceleration of sintering when increasing p_{CO} from 1.5 to 5 bar. Furthermore, the higher

diffusion barriers of $\text{Co}(\text{CO})_x$ species on $\gamma\text{-Al}_2\text{O}_3$ lead to significantly slower deactivation on this support compared to anatase and rutile TiO_2 . The mean initial particle diameter (D_{Co}) has a strong impact on deactivation rates, as the NP chemical potential ($\Delta\mu_{\text{Co}}$) profiles become steeper with decreasing particle size, thereby accelerating ripening. The width of the initial distribution plays a less prominent role, although narrower distributions exhibit somewhat slower deactivation, particularly during the early stages of the simulations. The results provide atomistic insight into CO-assisted sintering mechanisms, identifying subcarbonyl-mediated mass transport as a plausible contributor to catalyst deactivation under industrial conditions.

The second major focus of this thesis concerns Mn promotion. Following a DFT benchmark against experimental data, it is found that a value of the Hubbard parameter $U_{\text{eff}} = 2.5$ eV is adequate to describe the reactivity of Mn oxides. A correlation between the Mn magnetic moment and its formal oxidation state is further established, which is used to align theoretical models with experimental observations. A Genetic Algorithm (GA) combined with a Machine Learning Potential (MLP) is implemented to identify low-energy Mn structures of varying stoichiometries and loadings adsorbed on MC-derived Co NP models. A large dataset of $\text{Mn}_x\text{O}_y\text{H}_z$ clusters on periodic Co surfaces is constructed to refine the CHGNet potential, resulting in near-DFT accuracy at a significantly reduced computational cost. The resulting phase diagrams reveal that, following reduction, Mn preferentially adopts the $\text{MnO}\text{--}\text{MnO}_{1.5}$ phases, whereas FT conditions stabilize hydroxylated Mn structures. Increasing promoter loading favors formally more reduced Mn phases while simultaneously destabilizing surface-bound Mn species, suggesting an enhanced propensity for support interaction at elevated concentrations. In contrast, particle size and crystal phase exert only a marginal influence on Mn stability, with a slight thermodynamic preference observed for hcp NPs over their fcc counterparts. A pronounced preference of Mn for binding to the Co LCS is identified, a finding with direct implications for catalytic performance and stability. Finally, a charge-compensation mechanism is outlined in which the metallic Co NPs act as electron reservoirs, donating charge to the promoter clusters to keep Mn in its preferred 2+ oxidation state, even when stoichiometric considerations alone would suggest otherwise.

Finally, the electronic promotion effects of Mn are elucidated through DFT investigations of CO dissociation and oxygen removal pathways on pristine and Mn-promoted $\text{Co}(0001)$ surfaces. It is demonstrated through DFT-based thermodynamic analysis that the MnO_x motifs adsorbed on the Co terrace are highly flexible in regards to their O content. The results indicate that Mn lowers the overall barrier for CO dissociation by approximately 30 kJ/mol thanks to the emergence of particularly active sites at the Mn-Co interface, which is consistent with experimental observations of enhanced activity and C_{5+} selectivity. Furthermore, Mn is found to dramatically increase O removal rates by reducing the reaction barrier by about 50 kJ/mol, despite showing a higher tendency to retain water with respect to the pristine Co surface from a thermodynamic standpoint. The theoretical findings reproduce and rationalize trends obtained from our experimental collaborators, demonstrating the power of synergistic experimental–theoretical approaches.

Zusammenfassung

Die Fischer–Tropsch-(FT)-Synthese nimmt aufgrund ihrer Rohstoff flexibilität und ihrer Fähigkeit zur Herstellung langkettiger Kohlenwasserstoffe eine zentrale Stellung unter den möglichen Routen zur Produktion von Sustainable Aviation Fuels (SAFs) ein. Kobaltbasierten Katalysatoren kommt dabei die Rolle des industriellen Referenzsystems für die Niedertemperatur-FT-Synthese zu, da sie eine hohe Aktivität, Stabilität sowie eine ausgeprägte Selektivität gegenüber C5+-Produkten aufweisen. Dennoch begrenzen Katalysatordeaktivierung, Struktursensitivität und ein unvollständiges mechanistisches Verständnis der Promotoreffekte weiterhin mögliche Leistungssteigerungen. Insbesondere die Promotion durch Mangan (Mn) hat sich als wirksame Strategie zur Erhöhung der C5+-Selektivität etabliert, wobei die zugrunde liegende mechanistische und strukturelle Rolle des Mangans bislang nicht hinreichend verstanden ist.

Diese Arbeit präsentiert eine umfassende theoretische Untersuchung von reinen und Mn-promotierten Co-Katalysatoren für die FT-Synthese mit einem besonderen Fokus auf struktureller Modellierung. Es wird postuliert, dass ein Top-Down-Ansatz, bei dem katalytische Erkenntnisse aus strukturellen Merkmalen abgeleitet werden, umfassendere Einsichten liefern kann als konventionelle mechanistische Modellierungen, da viele der offenen Fragestellungen im Zusammenhang mit Co-FT-Katalysatoren über rein nanoskalige elektronische Effekte hinausgehen.

Im ersten Teil der Arbeit wird ein DFT-basiertes Monte-Carlo-Framework zur Modellierung von Kobaltnanopartikeln (NPs) als Funktion der Partikelgröße und der Metall–Träger-Wechselwirkungen (MSI) etabliert. Dieser Ansatz basiert auf einem aus DFT abgeleiteten Energiemodell, das in einem Monte-Carlo-Algorithmus eingesetzt wird, der wiederum Metallatome in einem festen fcc-3D-Gitter verteilt und nach energetisch günstigen Strukturen sucht. Das Energiemodell nimmt eine lineare Skalierung der Energie von Co-Atomen mit ihrer Koordinationszahl (CN) an und wird anhand von DFT-Rechnungen validiert. Die Simulationen zeigen im untersuchten Größenbereich einen systematischen Anstieg der Konzentration unterkoordinierter Stufen- und Knickstellen mit zunehmender Partikelgröße, im Einklang mit der experimentell beobachteten Struktursensitivität von Co-FT-Katalysatoren. Zunehmende Metall-Träger-Wechselwirkungen führen zu einer Abflachung der NPs, beeinflussen jedoch die Verteilung der aktiven Zentren kaum. Darüber hinaus wird eine umfassende Klassifikation der verschiedenen fcc-niedrigkoordinierten Zentren (LCS) etabliert, die zeigt, dass in kleinen Partikeln Kanten und Ecken dominieren, während bei größeren Partikeln Stufen- und Knickstellen überwiegen. Berechnungen zur direkten CO-Dissoziation belegen die Existenz besonders aktiver LCS, die bislang weitgehend übersehen wurden.

Anschließend werden CN-spezifische Energiekorrekturen zur Berücksichtigung der CO-Adsorption in das Energiemodell integriert. Es wird gezeigt, dass CO eine ausgeprägte Oberflächenrekonstruktion induziert, die durch eine Zunahme von B5-A-Stufenstellen auf Kosten von (111)- und (100)-Terrassen gekennzeichnet ist. Darüber hinaus senkt die CO-Adsorption die Oberflächenenergien der NPs erheblich und verändert dadurch maßgeblich die Stabilitätsprofile der Co-Nanopartikel. Ostwald-Reifungssimulationen zeigen eine drastische Beschleunigung des Sinterns bei einer Erhöhung von p_{CO} von 1,5 auf 5 bar. Darüber hinaus führen höhere Diffusionsbarrieren von $\text{Co}(\text{CO})_x$ -Spezies auf $\gamma\text{-Al}_2\text{O}_3$ zu einer deutlich langsameren Deaktivierung auf diesem Träger im Vergleich zu Anatas- und Rutil- TiO_2 . Der mittlere anfängliche Partikeldurchmesser D_{Co} hat einen starken Einfluss auf die Deaktivierungsraten, da die $\Delta\mu_{\text{Co}}$ -Profile mit abnehmender Partikelgröße steiler werden und somit die Reifung beschleunigen. Die Breite der anfänglichen Verteilung spielt eine weniger dominante Rolle, wenngleich engere Verteilungen insbesondere in den frühen Simulationsphasen eine etwas langsamere Deaktivierung zeigen. Die Ergebnisse liefern atomistische Einblicke in CO-induzierte Sintermechanismen und identifizieren Massentransport durch mobile $\text{Co}(\text{CO})_x$ Spezies als plausiblen Beitrag zur Katalysatordeaktivierung unter industriellen Bedingungen.

Der zweite Schwerpunkt dieser Arbeit liegt auf der Promotion durch Mn. Nach einem DFT-Benchmark gegen experimentelle Daten wird gezeigt, dass ein Wert des Hubbard-Parameters $U_{\text{eff}} = 2.5$ eV geeignet ist, die Reaktivität von Mn-Oxiden adäquat zu beschreiben. Zudem wird eine Korrelation zwischen dem magnetischen Moment von Mn und seinem formalen Oxidationszustand etabliert, die genutzt wird, um theoretische Modelle mit experimentellen Beobachtungen in Einklang zu bringen. Ein genetischer Algorithmus (GA) in Kombination mit einem Machine-Learning-Potential (MLP) wird implementiert, um energetisch günstige Mn-Strukturen unterschiedlicher Stöchiometrien und Beladungen auf MC-abgeleiteten Co-NP-Modellen zu identifizieren. Ein umfangreicher Datensatz von $\text{Mn}_x\text{O}_y\text{Hz}$ -Clustern auf periodischen Co-Oberflächen wird zur Verfeinerung des CHGNet-Potentials genutzt, wodurch eine nahezu DFT-genaue Beschreibung bei deutlich reduzierten Rechenkosten erreicht wird. Die resultierenden Phasendiagramme zeigen, dass Mn nach der Reduktion bevorzugt MnO – $\text{MnO}_{1.5}$ -Phasen bildet, während unter FT-Bedingungen hydroxylierte Mn-Strukturen stabilisiert werden. Mit steigender Promotorbeladung werden formal stärker reduzierte Mn-Phasen begünstigt, während gleichzeitig oberflächengebundene Mn-Spezies destabilisiert werden, was auf eine erhöhte Tendenz zur Wechselwirkung mit dem Träger bei höheren Konzentrationen hindeutet. Partikelgröße und Kristallphase haben dagegen nur einen geringen Einfluss auf die Mn-Stabilität, wobei eine leichte thermodynamische Präferenz für hcp-Nanopartikel gegenüber ihren fcc-Gegenstücken beobachtet wird. Darüber hinaus zeigt Mn eine ausgeprägte Präferenz für die Bindung an Co-LCS, ein Befund mit direkten Konsequenzen für Aktivität und Stabilität des Katalysators. Schließlich wird ein Ladungskompensationsmechanismus beschrieben, bei dem metallische Co-NPs als Elektronenreservoir fungieren und Ladung an die Promotorcluster übertragen, um Mn im bevorzugten Oxidationszustand $2+$ zu stabilisieren, selbst wenn rein stöchiometrische Überlegungen anderes nahelegen würden.

Abschließend werden die elektronischen Promotoreffekte von Mn durch DFT-Untersuchungen der CO-Dissoziation und der Sauerstoffentfernungsreaktionen auf reinen Co(0001)-Oberflächen sowie Co(001)-Oberflächen mit Mn-Promotion analysiert. Eine DFT-basierte thermodynamische Analyse zeigt, dass die auf der Co-Terrasse adsorbierten MnO_x-Strukturen hinsichtlich ihres Sauerstoffgehalts hochflexibel sind. Die Ergebnisse zeigen, dass Mn die Gesamtbarriere für die CO-Dissoziation um etwa 30 kJ/mol senkt, was auf besonders aktive Zentren an der Mn-Co-Grenzfläche zurückzuführen ist und mit experimentell beobachteter erhöhter Aktivität und C5+-Selektivität übereinstimmt. Darüber hinaus erhöht Mn die Sauerstoffentfernungsrate signifikant, indem die Reaktionsbarriere um etwa 50 kJ/mol reduziert wird, obwohl aus thermodynamischer Sicht eine stärkere Tendenz, Wassermoleküle zu binden, im Vergleich zur reinen Co-Oberfläche beobachtet wird. Die theoretischen Ergebnisse reproduzieren und rationalisieren experimentelle Trends aus der Zusammenarbeit mit unseren experimentellen Partnern und demonstrieren damit die Leistungsfähigkeit synergistischer experimentell-theoretischer Ansätze.

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Part I.

Introduction

1. Motivation

1.1. The Call for Sustainable Aviation Fuels

The development of the aviation sector throughout the past century has deeply transformed society. Having started as a niche endeavor for particularly risk-prone individuals, today flying is for many people an ordinary activity similar to traveling by bus. The rise of commercial aviation has dramatically accelerated the movement of people across the planet, leading to social and economic global integration that has greatly benefited humanity. Nowadays, aviation plays a prominent role in international trade, with 33% by value (and 1% by volume) of world cargo being transported through air. It was estimated that the total global aviation's economic output amounted to a staggering \$4.1 trillion in 2024, underscoring the central importance of this sector in modern society.[1]

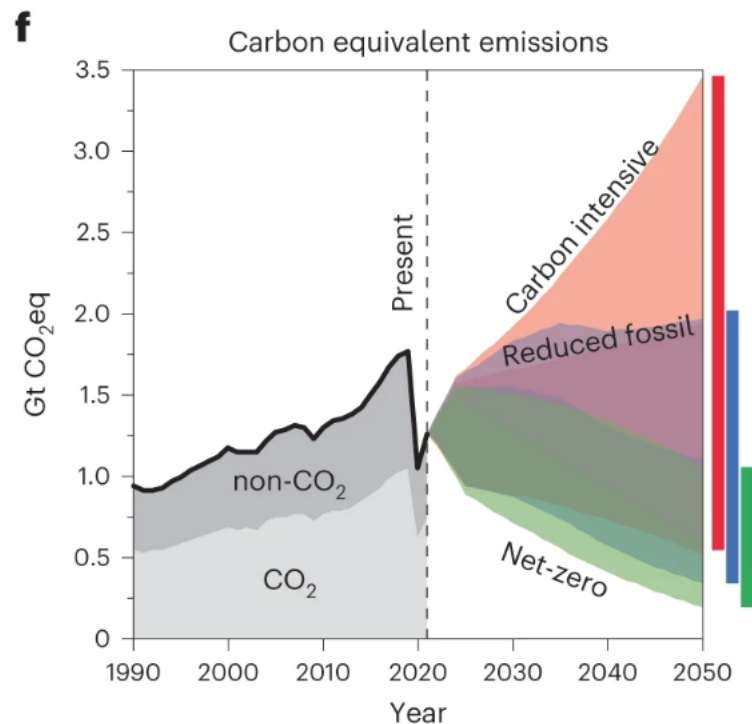


Figure 1.1.: The projected CO₂ equivalent emissions ranges in three different carbon consumption scenarios. Reprinted with permission from [2].

The heavy reliance of this industry on fossil fuels, however, makes it also one of the main sources of global greenhouse gas emissions. In 2019, aviation has accounted for 2.5%

of global CO₂ emissions, and despite dropping by about 40% in 2020 due to the COVID pandemic, in 2023 the emissions levels have reached once again 90% of the pre-pandemic peak.[3] Furthermore, as shown in Figure 1.1, projections according to a carbon intensive (i.e. business as usual) scenario indicate that the CO₂ equivalent emissions will increase dramatically, underscoring the urgency of reducing the carbon footprint of air transport.

Aviation is considered a hard-to-abate industry, as it is currently unfeasible to power aircraft solely with electricity, mainly due to the energy-density requirements that cannot be met with current battery technologies.[4, 5] Hence, the production of sustainable aviation fuels (SAFs) is regarded as the main option, at least in the short term, to decarbonize the sector. SAFs can be broadly defined as fuels with non-fossil origin, but can be further classified into biofuels and synthetic fuels. Biofuels are obtained from the processing of biomass, such as wood, agricultural residues, sewage, or municipal waste. The expression synthetic fuels, on the other hand, typically indicates fuels that are produced via chemical coupling of CO₂ and H₂, the first obtained via carbon capture and the second from water electrolysis carried out using a renewable energy source (e.g. wind or solar power), even though the definition may vary.

Currently, there are three main routes to produce SAFs. Hydrotreated esters and fatty acids (HEFA) are obtained when a fat or oil-rich feedstock undergoes a series of chemical reactions to yield jet fuels. These usually consist of hydrodeoxygenation, hydrocracking, isomerization and hydrogenation, often carried out over supported transition metal (TM) catalysts.[6, 7] HEFAs are currently the cheapest available SAFs, even though the process suffers from problems related to the feedstock that are limited availability in case exhausted oil or waste animal fat are used, or controversy over the fuel vs. food competition when vegetable oils are employed instead.[8] Another prominent route to SAFs is the so-called alcohol-to-jet (AtJ) process, where sugar-containing biomass is fermented to obtain alcohols, often ethanol or butanol, which are dehydrated and subsequently refined to paraffinic fuels via oligomerization and hydrogenation. The process is typically carried out over γ -Al₂O₃ or zeolitic catalysts for the dehydration step, while TM supported catalysts (often Ni-based) are employed for the oligomerization.[9, 10] The last route to SAFs is the Fischer-Tropsch (FT) synthesis, where syngas is catalytically converted into a wide range of hydrocarbons (HCs).[11–16] The FT synthesis is agnostic with respect to the source of the syngas, that has historically been fossil but that can also be renewable. In particular, FT can yield both synthetic and biofuels, depending on whether syngas is produced by carbon capture coupled with water electrolysis or biomass gasification. In the next section, we provide an overview of this long-established and yet still fascinating technology, that is the object of this thesis.

To achieve net-zero CO₂ emissions by 2050 in a business-as-usual scenario, it is estimated that roughly 20 EJ of SAFs should be made available in the market, which is about 4000 times the production of bio jet-fuels in 2019.[2] Since fuels constitute a considerable portion of airlines operating costs,[17] the fact that SAFs are 2.5–4.5 times more expensive than fossil kerosene is the main obstacle to their uptake in the aviation industry. Even though a concerted effort will likely be necessary to abate the costs of SAFs, increasing the efficiency of the current production technologies plays a pivotal role in addressing this task.

1.2. Fischer-Tropsch Synthesis

The Fischer-Tropsch process is named after the German scientists Franz Fischer and Hans Tropsch who first patented it in 1925. The enormous importance of FT lies in the fact that it enables production of liquid fuels from virtually any carbonaceous source, hence constituting an alternative to oil. Accordingly, the history of FT has been shaped by fluctuations in the crude oil market over the years. From its discovery until the end of World War II, the FT process was developed mainly in Germany, where strategic considerations dictated a reduction in the country's reliance on oil in favor of exploiting large domestic coal reserves. After the war, the discovery of large oil fields around the world guaranteed cheap and steady crude supplies, that resulted in diminished interest in FT. In this period, South Africa represented an exception, as the global political isolation prompted it to mitigate oil imports by converting its coal reserves into liquid fuels via FT. The oil crisis in the 70s and fears of fading oil reserves throughout the 80s and 90s renewed the interest in FT, that in the past three decades has been augmented by environmental concerns related to the effect of CO₂ emissions on global warming.[18] Furthermore, increasing fragmentation of the global economy triggered by international trade disputes and military conflicts might lead to additional interest in FT.

The chemistry of the FT synthesis is that of a surface polymerization reaction, and, as such, it consists of three main steps: chain initiation, growth and termination. In the first step, CO and H₂ adsorb on the catalyst surface, split and recombine to generate -CH_x species. It is heavily debated whether the CO dissociation step is direct or H-assisted, the latter occurring with formation of a formyl (HCO), or hydroxycarbonyl (COH) species prior to the C-O bond breaking.[19] The adsorbed O atoms obtained from CO dissociation are mostly hydrogenated and desorb as water in Co catalysts, with just traces of CO₂ being detected among the products. On the other hand, Fe catalysts display a higher water-gas-shift (WGS) activity, leading to higher selectivity to CO₂. [20] Regarding the chain growth step, two main mechanisms have been proposed that diverge regarding the nature of the species that are added to the growing chains. According to the carbide mechanism,[21, 22] this is a -CH_x fragment previously formed on the catalyst surface, with both -CH[23] and -CH₂[24] having been proposed. On the other hand, according to the CO insertion mechanism, as suggested by the name, it is a CO molecule inserts into a growing HC chain and whose C-O bond is subsequently cleaved. Notably, the CO insertion mechanism provides an alternative pathway also for CO dissociation. The chain termination step can occur via hydrogenation, β -elimination or CO insertion, leading to paraffinic, olefinic or oxygenate products, respectively.[25]

The product spectrum of FT approximately follows the Anderson-Schulz-Flory distribution, reinforcing the idea of a step-wise chain growth mechanism where one C is added at a time.[26, 27] Deviations from the ideal distribution, however, suggest a somewhat higher complexity of the reaction mechanism.[28] The C number distribution of the products is determined by the competition between chain growth and chain termination, that is quantified in the chain-growth probability commonly indicated as α . The main factors affecting the α value are relative H and C surface coverages as well as process conditions.

The syngas feed is commonly at a pressure of 20-30 bar with composition $\text{CO} : \text{H}_2 = 1 : 2$, and the reaction can be conducted in high-temperature (HT) or low-temperature (LT) regimes. Typical HTFT temperatures are in the 590-620 K range, leading to α values of 0.7-0.75 that mainly yield light HC products suitable for gasoline. Since most products are in the gas-phase at HTFT temperatures, the process is typically carried out in fluidized bed reactors. The LTFT reaction, on the other hand, takes place at temperatures in the 473-523 K range and can reach α values as high as 0.95. In this case, high C number products (C_{5+}) are mainly produced, and it is thus ideal when the aim is to produce jet fuels. Wax products as heavy as C_{100} are commonly obtained, that can further undergo hydrocracking to yield HC in the kerosene range. Due to the fact that LTFT is a three-phase system, slurry reactors are usually preferred.

The FT synthesis has been historically carried out over supported cobalt, iron, ruthenium and nickel catalysts. In practice, however, only the first two are employed in commercial plants.[29–31] Iron catalysts have been the first ones to be commercialized, are relatively cheap and highly versatile, as they can be employed both in HT and LTFT. Iron catalysts are characterized by a diverse phases landscape under operating conditions, as several Fe oxide and carbide compounds have been reported.[32–35] Among these, the $\chi\text{-Fe}_2\text{O}_5$ phase, also known as Hägg carbide, is often cited as one of the most active.[36, 37] Iron catalysts also display a certain WGS activity, that as mentioned earlier makes them more selective to CO_2 with respect to Co catalysts, but also somewhat more flexible in terms of the CO_2 content in the feed that they can sustain. This allows for looser feed purity requirements and makes Fe catalysts suitable to process syngas produced from different sources. Additionally, these catalysts are often heavily promoted with alkali metals, mostly sodium and potassium, that tend to suppress hydrogenation reactions and favor chain growth.[38, 39] In this context, recent computational studies have revealed that potassium enhances CO dissociation by increasing the electron density of the neighboring Fe atoms, which results in a higher population of the anti-bonding orbitals of the CO molecule and hence a weakening of the C-O bond.[40, 41] The main drawback of Fe catalysts, however, is that they are prone to deactivation that occurs in a number of ways, including carbon deposition, loss of active phase e.g. by oxidation, mechanical breakup and sintering.[20]

As mentioned above, the other type of commercial FT catalysts are Co-based, that are the ones discussed in this thesis and that we approach to describe in detail in the next section.

1.3. Co Fischer-Tropsch Catalysts

Co catalysts are employed only in LTFT and are more expensive than Fe ones. They are also more sensitive to poisons and require a high-purity feed. On the other hand, they are typically more stable under long operation regimes and yield higher C_{5+} selectivity. Co catalysts are commonly synthesized by impregnation of an oxidic support with a solution of a Co precursor (often Co nitrate), followed by a calcination step in air at 500-550 K that yields mostly the Co_3O_4 spinel phase. The calcined catalyst undergoes a further activation

step where it is reduced to Co^0 in a H_2 atmosphere at 650–700 K. A residual portion of Co^{2+} is usually detected after activation, whose amount depends on the initial particle size distribution and support material. Nevertheless, the residual Co^{2+} species can be further reduced during FT. Co catalysts are routinely promoted with a minute amount of a noble metal such as Platinum or Ruthenium to improve reducibility. As opposed to Fe catalysts, it is widely accepted that the active phase under operation is Co^0 .

Structure sensitivity. FT Co catalysts display strong structure sensitivity, that consists of an increase of turnover frequency (TOF) with particle size (D_{Co}) upto ~ 10 nm, that stays constant thereafter.[20, 42–51] The size-dependency of the TOF of Co FT catalysts as reported across several studies is shown in Figure 1.2. This type of structure sensitivity mirrors the increase of surface concentration of undercoordinated step and kink sites as the metal nanoparticles (NPs) grow bigger, and it is telling regarding the nature of the rate-determining step in this size range. Step and kink sites, in fact, are the ones that can activate strong π bonds such as those of CO, since they allow the dissociating molecule to coordinate to several metal atoms simultaneously, which is necessary to stabilize the transition state (TS). The experimental observations suggest that, on NPs below 10 nm, there are not enough sites that can catalyze CO splitting, that hence becomes a bottleneck in the reaction network. The structure insensitivity reported for $D_{\text{Co}} > 10$ nm suggests that hydrogenation reactions might become rate-determining from this threshold onward, as they typically do not require specific surface configurations.[52, 53] Importantly, the same kind of structure sensitivity trends are reported across different supports, indicating that sites at the metal-support interface do not play a significant role in the reaction. Besides, contrary to the TOF, the fraction of these sites decreases with increasing particle size, which suggests that they are not particularly active during FT.

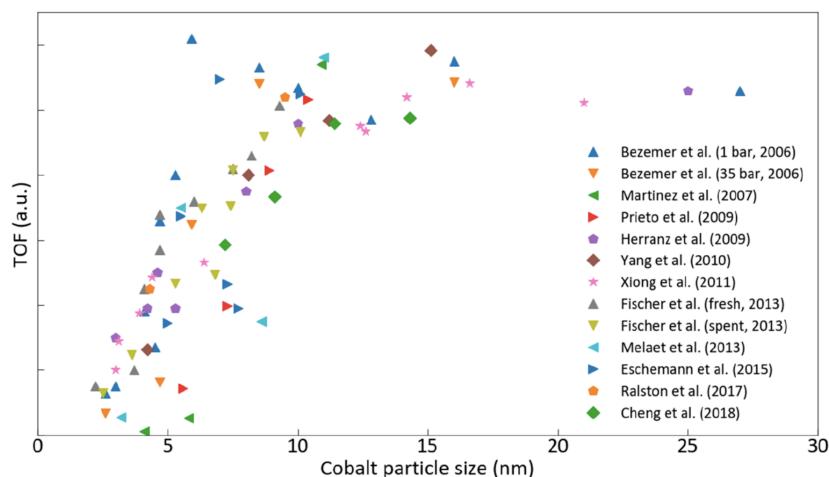


Figure 1.2.: The size dependency of the TOF for Co FT catalysts reported across different studies. Reprinted from Ref. [51] with permission. Copyright 2023 American Chemical Society.

Competition between crystal phases. A further critical aspect of Co FT catalysts is the coexistence of face-centered cubic (fcc) and hexagonal close-packed (hcp) NPs. Bulk Co assumes the hcp crystal structure at FT conditions, as the hcp→fcc transition occurs at 700

K, well above the temperature in the LTFT regime.[54, 55] Nonetheless, Co NPs behave differently from the bulk metal as below 20 nm they are predominantly in the fcc phase, likely due to surface energy effects.[56] In practice, technical catalysts always contain a mixture of the two phases, whose proportions can be tuned by tailored synthesis methods. While conventional Co catalysts prepared according to the procedure mentioned above are typically fcc-rich, it has been reported that the amount of the hcp phase can be boosted by favoring the formation of hexagonal instead of cubic CoO in the fresh catalyst.[57] An alternative pathway to predominantly hcp catalysts is the so-called reduction-carburization-reduction (RCR) synthesis methods, that is a three-steps process during which the catalyst precursor is first reduced, subsequently carburized to yield Co_2C and finally reduced again.[58–60] Reduction of the Co carbide phase yields predominantly hcp-Co likely because of the similarity of the two crystal structures, as Co_2C is equivalent hcp-Co with the addition of interstitial carbon. Importantly, the two phases display different reactivities, as hcp-Co provides higher TOF and C_{5+} selectivities than fcc.[57, 58] The enhanced activity of hcp Co NPs may arise from the higher density of CO splitting sites relative to their fcc counterpart. In fact fcc-Co NPs mainly expose the (111) facet that displays prohibitively high CO dissociation barriers, while hcp-Co NPs only expose about 20% of the analogous (0001) surface.[61, 62] Alternatively, DFT calculations carried out by Liu et al.[63] indicate that hcp might be more active because, unlike fcc, it possess extraordinarily active sites.

Deactivation. The deactivation of Co catalysts is believed to occur via an interplay of different mechanisms, where each can be attenuated or enhanced depending on process conditions and catalyst design. It has been consistently observed, however, that technical Co FT catalysts under industrial conditions display an initial fast deactivation within the first 10-20 days of operation, followed by a constant and slow long-term deactivation.[64] The initial deactivation has often been ascribed to catalyst sintering. It is heavily debated in the literature whether the predominant sintering mechanism involves particle migration and coalescence (PMC)[65–68] or Ostwald ripening.[69–72] While both mechanisms can be favored based on process conditions, support material and particle size distribution, Kirstamurthy et al.[73] have obtained conclusive evidence of Ostwald ripening type of sintering on their flat-model SiO_2 -supported Co catalyst. Additionally, it was shown that sintering on a $\gamma\text{-Al}_2\text{O}_3$ -supported catalyst only occurs in the presence of CO,[71] which confirms the hypothesis of a CO-assisted sintering mechanism. While CO could also favor PMC by lowering Co adhesion on the support, it is speculated that its main effect could be to form mobile subcarbonyl species that contribute to sintering via Ostwald ripening.[74] In the presence of CO, increasing H_2O partial pressure further enhances the sintering process, even though no conclusive hypothesis has been formulated to date on why this is the case.

Another prominent deactivation mechanism is carbon deposition. Albeit carbon is a natural FT product that comes from the dissociation of CO, under conditions of depleted H_2 adsorbed C monomers can give rise to effects that are detrimental for catalysts activity. In particular, C can diffuse into Co subsurface layers significantly hindering the reactivity of Co surface atoms, that become less prone to accept and back-donate electron density from/to CO molecules.[75] Additionally, DFT calculations indicate that adsorbed C can induce a clock-reconstruction of the fcc(111) and (100) surfaces that likely hinders CO

adsorption.[76] The ability of adsorbed C to significantly reconstruct Co terraces has been additionally confirmed via molecular dynamics simulations.[77] Further C buildup due to lack of H₂ eventually causes NPs carburization yielding Co₂C, which is widely regarded as inactive for the FT synthesis. We note, however, that *ad-hoc* synthesized Co₂C nanoprisms were recently shown to be active for the production of lower olefins and higher alcohols.[78, 79] Nonetheless, abnormal levels of H₂ depletion are necessary to trigger these effects, that hence are not expected to extensively take place under ordinary FT operation. It is plausible, therefore, that the long-term deactivation mode mentioned above is due to yet another C species, i.e. polymeric carbon that grows slowly but steadily and eventually causes surface fouling and deactivation.[80, 81] In particular, Moodley et al.[64] observed a slow buildup of such polymeric C species over long time of operation which was linked to protracted deactivation.

Even though sintering and carbon deposition are the two dominant deactivation mechanisms for Co catalysts, a third one that is often discussed is Co reoxidation. This is speculated to happen especially in high CO conversion (X_{CO}) regimes, where the large p_{H_2O}/p_{H_2} ratios result in markedly oxidizing conditions. The main driving force of this phenomenon is the lower surface energy of CoO with respect to Co⁰, that is stronger the smaller the Co NPs due to increasing surface to volume ratios.[82] Even though several studies have mentioned Co reoxidation as a possible deactivation mechanism, eventually strong evidence that this can be ruled out under industrial FT conditions came about.[83] On the other hand, Co oxidation leading to metal-support compounds formation is thermodynamically more favorable than to CoO.[84–86] Among the most common supports of Co catalysts, namely γ -Al₂O₃, α -SiO₂ and TiO₂, Co⁰ oxidation to CoAl₂O₄ is the most exothermic, followed by that to CoTiO₃ and Co₂SiO₄, with the latter being markedly endothermic. Nonetheless, experimental work has demonstrated only marginal CoAl₂O₄ formation over long industrial FT operation,[87] possibly due to the high kinetic barriers preventing the solid-state reaction from happening.[88] It is likely that the portion of Co-support compounds commonly found in Co catalysts hence does not form during FT but rather during reduction, where the reaction of CoO with the support can be accelerated by the higher temperatures. These compounds do not reduce during operation, and hence the Co atoms they incorporate are lost for the purpose of the FT synthesis. However, it has been postulated that these compounds might form at the interface between Co NPs and the support and tune the interactions between the two phases, ultimately leading to enhanced sintering resistance.[89]

Finally, poisoning is also a possible deactivation mechanism for Co FT catalysts.[90] Sulfur poisoning, as for most metal catalysts, is considered the most critical because of its marked detrimental effect on activity, likely due to blockage of surface sites and inhibition of CO adsorption.[91, 92] Poisoning by nitrogen compounds has also been investigated, even though it seems to become relevant over protracted catalyst exposure and to contribute to slow, reversible deactivation.[93] Additionally, alkali and alkaline earth metals are often cited as possible poisons for Co FT catalysts. While these substances can be detrimental for activity, they are known to also increase C₅₊ selectivity, and it is postulated that moderate amounts can actually be beneficial for catalyst performance.[94, 95] Overall, while catalyst poisoning could significantly affect FT operation depending on the carbonaceous source

and should be hence taken into account in process design, it seems like it can be effectively prevented with adequate uphill syngas purification.

1.4. Mn Promotion

As mentioned in Section 1.1, the main obstacle to replacing fossil kerosene with SAFs is that the latter are significantly more expensive. Overcoming this limitation requires abating the costs of SAFs via a multi-pronged approach, in which catalyst optimization plays an important role. In this context, Mn promotion has emerged as an active area of research for the improvement of Co FT catalysts due to its ability to increase the yield of valuable C_{5+} products.[96]

Albeit a plethora of different synthesis routes for Mn-promoted Co catalysts have been proposed in the literature, one of the most common is coprecipitation, where the oxidic support is impregnated in a solution containing salts of both Co and Mn. Alternatively, the use of two or more subsequent impregnations with either one of the two solutions is also a common procedure. After drying and calcination, mixed $Co_{3-x}Mn_xO_4$ NPs with spinel crystal structure are commonly obtained, that are typically smaller than pure Co ones, leading to higher active phase dispersion. The Co-Mn mixed particles are harder to reduce as highlighted by temperature-programmed reduction (TPR) experiments that report a shift of the second reduction peak to higher temperatures, an effect that becomes more pronounced with increasing Mn loading.[97] After reduction, the catalyst displays Mn species closely associated with Co^0 NPs. This has been frequently observed in studies employing Scanning Transmission Electron Microscopy (STEM) Spectroscopy with elemental mapping, of which one example is shown in Figure 1.3.[98] It has been demonstrated that the intimate contact between the two species is closely related to the promotional effects.[99]

At low promoter loadings Mn predominantly forms highly dispersed clusters associated with Co, while larger Mn conglomerates accumulated around the Co NPs start to appear as more promoter is added to the system. Accordingly, the surface of Co NPs becomes partially covered by Mn,[100] as confirmed by decreased H_2 uptake with increasing promoter loading.[97, 98] Further experimental characterization indicates that Mn is predominantly in the divalent state in the activated catalyst.[98, 101, 102]

The promotional effects of Mn are both structural and electronic. Regarding the first, Mn has been shown to increase sintering resistance, that could be attributed to a stronger anchoring of Co NPs to the support mediated by Mn.[58, 103] Additionally, by covering the Co surface, Mn might also hinder the formation of Co adatoms and subcarbonyl species and hence inhibit sintering via Ostwald ripening. On the other hand, Mn has also been reported to enhance Co_2C formation,[103, 104] that can be explained in light of the frequently reported higher C coverage on Mn-promoted catalysts, since more loose C monomers can diffuse into the Co NPs causing carburization.

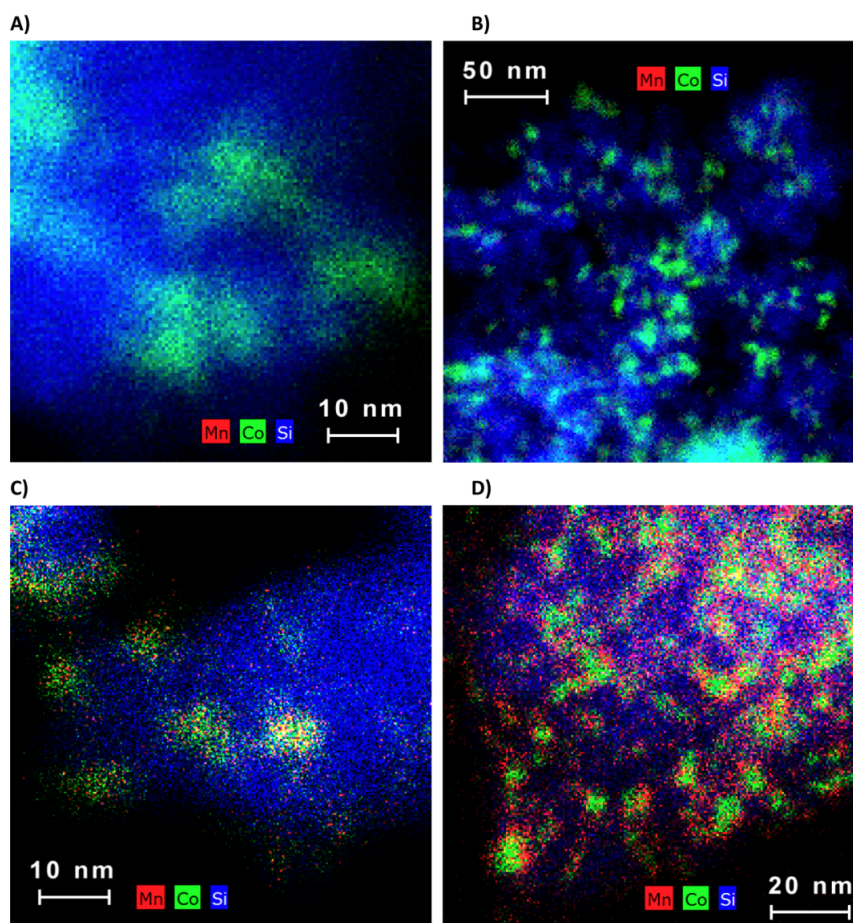


Figure 1.3.: STEM-EDS elemental maps of Co–Mn catalysts with bulk Mn/Co atomic ratios of (A) Mn/Co = 0.01, (B) Mn/Co = 0.05, (C) Mn/Co = 0.1, and (D) Mn/Co = 0.5. Reprinted from Ref. [98] with permission. Copyright 2015 American Chemical Society.

From an electronic standpoint, Mn typically enhances C_{5+} selectivity, which is the reason why it is regarded as an attractive promoter to maximize the yield of jet fuels. The increase in C_{5+} selectivity is often accompanied by an increase in TOF, even though the latter effect is not as common as the former. Albeit there is currently no consensus on the underlying mechanism enabling the electronic promotion, different studies indicated that Mn enhances CO dissociation.[98, 101, 105, 106] In particular, in the study by Johnson et al. enhanced CO dissociation upon Mn promotion was demonstrated through a combination of kinetic analysis, CO temperature-programmed desorption, direct measurements of CO disproportionation, and in situ infrared spectroscopy, all of which consistently indicate strengthened CO adsorption and weakened C–O bonds at Co–MnO interfacial sites. The authors postulated that the reason for the enhanced dissociation is a Lewis acid-base interaction between the Mn^{2+} ions and $O^{\delta-}$ atoms of the CO molecules, which weakens the C–O bond and favors its cleavage. Similar results were obtained by Kimpel et al.[101] that demonstrated enhanced CO dissociation upon Mn promotion by a reversal of the CO reaction order, increased CH_x surface coverage despite exceptionally high CO coverages measured by SSITKA, a substantially reduced onset temperature for CO dissociation ob-

served by operando IR spectroscopy, and DFT calculations showing a lower activation barrier for H-assisted CO dissociation at Co–MnO interfacial oxygen vacancies. Alternatively, it has been proposed that Mn may facilitate O removal, enabling faster regeneration of the active sites and hence increased TOFs.[97] We note that while increased C_{5+} selectivity upon Mn promotion is rather transversal across different catalyst, increasing promoter loading eventually leads to a decrease of activity, for which a maximum is often observed at Mn/Co molar ratios of 0.05–0.15.[97, 98, 106] This is compatible with the hypothesis of a balance between two opposite effects, namely promotion and blockage of Co sites, that is graphically depicted in Figure 1.4 adapted from Ref. [98]. This scenario implies that there is an optimal Mn loading for which the number of promoted interfacial sites is maximized without significantly obstructing cobalt surface; further Mn addition above this optimum, on the other hand, becomes counterproductive as it leads to partial encapsulation of the Co NPs.

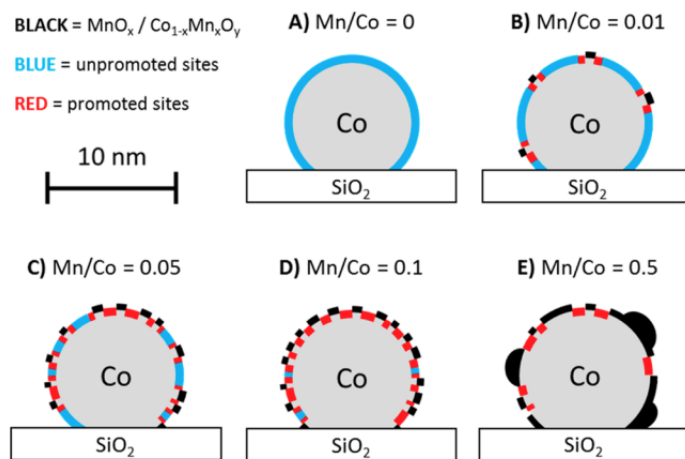


Figure 1.4.: STEM-EDS elemental maps of Co–Mn catalysts with bulk Mn/Co atomic ratios of (A) Mn/Co = 0.01, (B) Mn/Co = 0.05, (C) Mn/Co = 0.1, and (D) Mn/Co = 0.5. Reprinted from Ref. [98] with permission. Copyright 2015 American Chemical Society.

To conclude this section, we point out that despite Mn-promoted catalysts are now employed in industrial FT operation, there is still a lack of consensus regarding the underlying promotional mechanism. This is partly due to the complexity of the system, that makes it difficult from an experimental perspective to discern between the multitude of different interconnected effects. In this context, we believe that tackling the problem from the theoretical perspective can prove helpful, as it allows for a more precise study of each individual effect and might ultimately yield a clearer overview of the system under scrutiny.

1.5. Theoretical Modeling of Co Fischer-Tropsch Catalysts

Modeling of pristine Co catalysts. Density functional theory (DFT) calculations have played a central role in advancing the molecular-level understanding of cobalt-based FT synthesis.

Seminal theoretical studies investigated the mechanistic aspects of the reaction, with a special focus on CO dissociation. It became clear early on that the barriers for direct CO dissociation on Co(111) and (0001) were too high to explain the experimental apparent activation energies, which prompted several studies to search for alternative pathways for the initial step of the process. One hypothesis that soon emerged was that CO dissociation does not take place on the Co terraces, but rather on stepped surfaces that were identified as defect sites. In particular, the studies by Gong et al.[107] and by Ge and Neurock[62] demonstrated that the barriers for CO dissociation are significantly lower on such surface conformations. Nonetheless, there was skepticism regarding the actual presence and availability of these sites under FT conditions, which led several works to investigate alternative pathways for CO dissociation on the Co terraces.

DFT calculations by Inderwildi et al.[108] showed that CO bond cleavage is significantly more facile upon CO hydrogenation to HCO and H₂CO species, that hence supported the hypothesis of a H-assisted CO dissociation mechanism. Since then, H-assisted pathways have been extensively investigated, also considering other intermediates such as COH and HCOH species.[19, 109, 110] There are, however, two main recurring issues with the calculation of H-assisted pathways that, if not addressed, can significantly alter our understanding of the reaction energetics. The first is that even though the barriers for the CO bond cleavage are rather low starting from the hydrogenated intermediates, their formation is usually markedly endothermic, making the overall reaction barrier on the Co terraces still too high with respect to experimental measurements. Additionally, several studies did not include the Zero-point energies (ZPE) contributions to the reaction energetics, which further destabilize the hydrogenated species. In fact, the formation of high frequency bonds can cause a positive Δ ZPE contribution to the formation energy of the hydrogenated species as high as 0.2 eV per C–H or O–H bond formed, that are typically in the 3000 cm⁻¹ frequency range. This can significantly increase the overall reaction barriers, especially when the pathway involves more than one hydrogenation. Not considering these two effects has led different studies to predict artificially low reaction barriers for H-assisted CO dissociation, wrongly reinforcing the idea that this is the predominant mechanism for C monomer formation. A more recent study by Petersen et al.[111], that accounted for ZPE contributions, suggests that direct CO dissociation is preferred over the H-assisted routes on fcc step and kink sites. Nonetheless, hydrogen plays a pivotal role in the regeneration of the active sites as the reaction products must be hydrogenated before they can desorb, explaining the experimentally observed positive reaction order with respect to the H₂ partial pressure.[112]

CO insertion has likewise been explored with DFT calculations and found to yield reasonable barriers on Co(0001) of roughly 150 kJ/mol.[61] Nonetheless, the proposed pathway involved several hydrogenation steps while ZPE contributions were likely not included, implying that the actual overall energy barrier is probably significantly higher. Furthermore, later microkinetic studies based on DFT calculations concluded that the CO insertion mechanism is not consistent with experimental kinetic rate expressions.[113] More recent microkinetic models increasingly support carbide-type chain growth involving O-free C₁ species (CH_x^{*} or C^{*}) as the dominant pathway on cobalt.[114–116]

Theoretical studies eventually evolved from arbitrary periodic surface models to active sites representations grounded on the morphology of Co NPs. This became urgently needed as clear trends regarding structure sensitivity and crystal phase dependency started to emerge from a plethora of experimental works. Liu et al.[63] calculated the Wulff equilibrium shapes of fcc and hcp-Co NPs and investigated direct and H-assisted CO dissociation pathways on the exposed surface sites. Their results suggested that hcp-Co NPs are more active than their fcc counterparts because they possess special sites where the CO dissociation barriers are significantly lower than on any of the investigated fcc configurations. Theoretical calculations were additionally employed to elucidate the structure sensitivity of Co catalysts, which was done by predictions of low-energy structures of Co NPs with increasing size. The Wulff construction was not a suitable approach due to its inherent size-independency, and therefore more sophisticated computational techniques were elaborated. The first to address this task were van Helden et al., that employed Monte Carlo (MC) simulations integrating a lattice model to resolve the morphologies of fcc-Co NPs.[117] More recently, they applied their methodology to study also hcp-Co NPs.[58] Later on, Agrawal et al.[118] and van Etten et al.[119] resorted to molecular dynamics simulations to model the structures of Co NPs that were obtained via a simulated annealing equilibration procedure. In a later work, van Etten et al. additionally included the effect of the support in their simulations.[120] Despite following different strategies, that will be more thoroughly described in Chapter 3, all these studies observed a marked increase of step sites with particles size, that was linked to their ability to dissociate CO. Hence, these works suggest that CO dissociation is the rate-determining step at least for particles smaller than 10 nm.

Theoretical insights into Mn promotion. DFT has also been employed to shed light on the promotional mechanism of Mn. These calculations are far exceeded by those carried out for pristine Co catalysts in terms of volume, variety and level of detail, but nonetheless reveal insightful energetic trends. The first study that included DFT calculations on Mn promotion was one by Pedersen et al.[121], where metallic Mn was embedded in a Co(111) facet either as surface or subsurface layer. This work reported enhanced CO adsorption and dissociation in the Mn-promoted systems, even though these results have limited transferability to actual technical catalysts, where Mn is found in the divalent state.

Gupta et al.[122] considered a Mn_4O_4 cluster, that was first optimized in the gas phase yielding a ring structure that was subsequently adsorbed on a Co(0001) terrace. They observed slightly stronger CO adsorption in the presence of Mn, which also significantly lowered the barrier for direct and H-assisted via the hydroxycarbonyl intermediate (COH) CO dissociation. Nonetheless, the investigated CO dissociation mechanisms on the Mn-promoted surface yielded roughly the same barrier as the most favorable formyl (HCO) route on the bare Co surface, somewhat confuting the claim of enhanced CO dissociation upon Mn promotion. Almost at the same time, Zhang et al.[123] published a comparative DFT and kinetic Monte Carlo (kMC) study of pristine and Mn-promoted Co(0001), where the promoter was represented as a linear Mn_8O_8 periodic structure. They found that Mn facilitates all the investigated CO dissociation routes as well as O removal via disproportionation of two adsorbed hydroxyl groups, drastically increasing the rates of CO consumption of the catalyst. In a later work, Tucker et al.[97] investigated the stability

of different mononuclear Mn oxidic clusters adsorbed on Co(111), and predicted through DFT-based thermodynamic analysis that a linear O-Mn-O structure would be the most favorable one under industrial FT conditions. Even though a 4+ Mn oxidation state was expected based on cluster stoichiometry, it was postulated that electron density donation from the Co surface might keep Mn in the experimentally observed 2+ oxidation state. Further investigation of reaction energetics indicated that Mn would facilitate O removal but not CO dissociation.

More recently, Kimpel et al.[101] investigated the catalytic activity of a Mn_4O_4 cluster adsorbed on Co(0001). Importantly, they employed a genetic algorithm (GA) as a global optimization (GO) method to carry out unbiased sampling of the potential energy surface (PES), and identified a global minimum structure (GM) identical to the one proposed by Gupta. They investigated a reaction mechanism involving the formation of an O vacancy on the oxidic cluster, that is then filled by a dissociating CO molecule. They calculated extremely low energy barriers for the formyl route to CO dissociation of only 0.98 eV, which is significantly lower than for unpromoted Co terraces, even though they likely did not include ZPE contributions. Furthermore, they found the formation of the O vacancy to be endothermic but kinetically accessible via disproportionation of adsorbed hydroxyl groups. Finally, in a recent work Chen et al.[124] modeled a Mn promoted Co(0001) terrace, where two rows of Co atoms were removed to make space for a Mn oxidic cluster containing four Mn atoms, whose structure was optimized using a minima hopping algorithm. They found that (both direct and H-assisted) CO dissociation, as well as C-C coupling reactions are more favorable on the promoted Co surface, and additionally noted that chain termination might be inhibited by the lower availability of hydrogen that is sequestered by the Mn structure.

Overall, the majority of the discussed studies support the conclusion that Mn enhances CO dissociation, in agreement with experimental evidence. However, these works are largely based on simplified models, that have often been arbitrarily chosen. This has caused them to sometimes draw qualitatively different conclusions, ultimately clouding our mechanistic understanding of Mn promotion. A holistic theoretical characterization of Mn structures on Co NPs is therefore essential to revert this tendency, as it would help developing a broader catalytic picture and a coherent theory of Mn promotion.

1.6. The Scope of this Work

In this thesis, we adopt a theoretical approach to elucidate key aspects of the reactivity and stability of pristine and Mn-promoted Co FT catalysts. Rather than pursuing a detailed mechanistic analysis of the FT reaction network, we deliberately focus on a complementary perspective. Mechanistic aspects have already been partly addressed in previous theoretical studies, and, given the intrinsic complexity of the system, an exhaustive treatment would risk becoming entangled in a multitude of variables, potentially obscuring the broader catalytic picture. Instead, our approach is centered on the structural modeling of the catalyst. By constructing comprehensive structural models, we obtain a bird's-eye view of

the behavior of both promoted and unpromoted Co FT catalysts, enabling us to identify important qualitative trends that would likely remain inaccessible in a purely mechanistic investigation.

The results of this thesis are organized into three main chapters. In Chapter 3, we establish a DFT-based MC methodology to model metal NPs as a function of particle size and metal–support interactions (MSI), using fcc-Co and representative FT oxidic supports as case studies. We further perform an extensive characterization of the plausible active sites emerging from these models, track their concentration as a function of particle size, and probe their reactivity by calculating direct CO dissociation pathways.

In Chapter 4, the methodology is extended to account for the FT gas phase, allowing us to investigate how variations in CO partial pressure affect the structure and stability of fcc-Co NPs. In the second section of this chapter, we perform Ostwald ripening simulations to study catalyst deactivation over industrially relevant time scales as a function of CO partial pressure, support, and initial particle size distribution. This analysis combines the results of MC simulations with DFT calculations of the formation and diffusion of Co subcarbonyl species.

Chapter 5 focuses on Mn promotion. In the first section, we establish optimal computational settings for DFT calculations of Mn-promoted Co surfaces and derive a correlation between the Mn atomic magnetic moment and its formal oxidation state, which is subsequently used to align our models with experimental observations. In the second section, we develop a GA that exploits the computational efficiency of machine-learning potentials to generate low-energy models of Mn-decorated Co NPs. This approach enables a systematic exploration of Mn-induced structures and their stability as a function of stoichiometry, Mn loading, Co particle size, and crystal phase, on length scales inaccessible to state-of-the-art DFT calculations while simultaneously accounting for multiple factors that are often neglected. In the final section, we elucidate the electronic promotion effects of Mn by calculating CO dissociation and O removal pathways on pristine and Mn-promoted Co(0001) single crystals. These results reproduce and rationalize, from a mechanistic perspective, experimental findings obtained from our partners at Helmholtz-Zentrum Berlin, highlighting the potential of synergistic experimental–theoretical approaches.

This thesis demonstrates how advanced atomistic modeling can be used to address the multiscale complexity of FT catalysis beyond the scope of conventional mechanistic approaches. By integrating first-principles calculations with MC simulations, genetic algorithms, and machine-learning potentials, it provides transferable insights and methodologies for understanding and rationally designing pristine and Mn-promoted Co catalysts.

2. Theory

2.1. Electronic Structure Theory

The discussion regarding Hartree-Fock and Density Functional Theory is articulated along the lines of Chapters 5 and 7 of the 4th edition of the book *"Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics"* by Errol G. Lewars,[125] that in our opinion are exceptionally clear and informative regarding the subject we are about to approach.

2.1.1. Quantum Chemistry

According to quantum mechanics, the energy of a system can be known by solving the time-independent Schrödinger equation:

$$\hat{H}\Psi(\mathbf{r}) = E \Psi(\mathbf{r}) \quad (2.1)$$

Where $\hat{H}$ is the energy operator, also known as the Hamiltonian, $\Psi(\mathbf{r})$ is the wavefunction that depends on the vector of the positions of the particles in the system $\mathbf{r}$ and E is the energy of the system. Amongst the multitude of chemical systems, however, the Schrödinger equation can be solved analytically only for the H atom. This is because, when considering any other chemical environment, we immediately incur in the so-called *many-body problem*, a mathematical conundrum that arises whenever a system with more than two interacting bodies is to be treated. The first simplification that can be used to circumvent this issue is to consider protons as steady particles around which electrons orbitate. This is known as the Born-Hoppeneimer approximation, and is justified by the fact that protons are significantly (1837 times) heavier than electrons. Within this approximation, it is possible to focus on the electronic Schrödinger equation, that for the Helium atom is:

$$\left[\frac{-\hbar^2}{8\pi^2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0r_1} - \frac{Ze^2}{4\pi\epsilon_0r_2} + \frac{e^2}{4\pi\epsilon_0r_{12}} \right] \Psi = E\Psi \quad (2.2)$$

The term in bracket is the Hamiltonian operator, within which, from left to right, we find the kinetic energy of the two electrons, the Coulombic potential energy of attraction between the electrons and the nucleus (2nd and 3rd terms) and the electron-electron

repulsion energy. Nevertheless, within the Born-Oppenheimer approximation, only one-electron systems such as the H_2^+ molecule can be treated in addition to the H atom. Already when considering the Helium atom, in fact, the term relative to the inter-electronic distance r_{12} triggers once again the many-body problem. In the following text, it will be shown the strategy elaborated by Hartree, and improved by Slater, Pauling and Fock, to overcome this limitation.

2.1.2. Hartree-Fock Approach

Hartree addressed this difficulty by proposing that the many-electron wavefunction may be written as a product (also called Hartree product) of n one-electron wavefunctions (or spatial orbitals), where n denotes the number of electrons in the system:

$$\Psi_0 = \psi_0(1)\psi_0(2)\psi_0(3)\dots\psi_0(n) \quad (2.3)$$

As indicated by the subscripts in the above equation, the Hartree method starts from an initial guess (or 0th order) wavefunction, that is iteratively refined to obtain an improved description of the system under scrutiny. Instead of solving one n -electrons Schrödinger equation, by using this expedient the problem simplifies to solving n one-electron Schrödinger equations, where each electron feels the repulsion of a smeared out electrostatic field equal to the products of all the other one-electron wavefunctions. At each iteration, the k th order $\psi_k(1\dots n)$ one-electron wavefunctions are solved to yield Ψ_{k+1} . The procedure is repeated until the refined wavefunction is identical within certain convergence criteria to the one from the previous iteration, i.e. when the field of Ψ_{k+1} is consistent with that of Ψ_k . For this reason, this procedure is often indicated as the *self-consistent field* (SCF) method.

The Hartree approach, however, suffers from two main shortcomings: the first is that it does not take into account electrons spin, and the second is that the Hartree wavefunction is symmetric with respect to the exchange of the positions of two electrons, in contrast to the fermionic nature of electrons revealed by experiments that dictates that the wavefunction should actually be antisymmetric. The Hartree method has been improved in the Hartree-Fock (HF) analysis, developed by Pauling, Slater and Fock. The first modification of the Hartree theory consists in considering, in place of spatial orbitals, so called spin orbitals in which only one electron can be accommodated. Two spinorbitals are obtained from each spatial orbital via multiplication by the two spin functions α and β , which ensures that only two electrons of opposite spin can be placed in one spatial orbital. Furthermore, Pauling and Slater pointed out that instead of writing the polyelectron wavefunction as a simple product of the one-electron wavefunctions, it may be better approximated by a *Slater determinant*, where the elements of the first row are all the different spinorbitals assigned to electron 1, those of the second row are all the different spinorbitals assigned to electron 2 and so on. The Slater determinant for a four-electron system is found below:

$$\Psi' = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \psi_2(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \psi_2(2)\beta(2) \\ \psi_1(3)\alpha(3) & \psi_1(3)\beta(3) & \psi_2(3)\alpha(3) & \psi_2(3)\beta(3) \\ \psi_1(4)\alpha(4) & \psi_1(4)\beta(4) & \psi_2(4)\alpha(4) & \psi_2(4)\beta(4) \end{vmatrix} \quad (2.4)$$

Where the prefactor $\frac{1}{\sqrt{4!}}$ is a normalization constant. Writing the polyelectron wavefunction as a Slater determinant ensures that its antisymmetric character is respected, as switching the positions of two electrons is equivalent to switching two rows of the matrix, leading to a change of sign of the determinant. Writing the extended electronic Hamiltonian (in atomic units) for a generic $2n$ electron systems (where μ is the subscript for the generic nucleus) leads to the following expression:

$$\hat{H} = \sum_{i=1}^{2n} -\frac{1}{2} \nabla_i^2 - \sum_{\mu,i} \frac{Z_\mu}{r_{\mu i}} + \sum_{ij} \frac{1}{r_{ij}} \quad (2.5)$$

Substituting Equations 2.4 and 2.5 in the expression for evaluating the energy of the system below yields:

$$E = \int \Psi^* \hat{H} \Psi d\tau \quad (2.6)$$

After numerous manipulations, the following expression for the energy is obtained:

$$E = 2 \sum_{i=1}^{2n} H_{ii} + \sum_{i=1}^n \sum_{j=1}^n (2J_{ij} - K_{ij}) \quad (2.7)$$

Where

$$H_{ii} = \int \psi_i^*(1) \hat{H}^{core}(1) \psi_i(1) dv \quad (2.8)$$

And

$$\hat{H}^{core}(1) = -\frac{1}{2} \nabla_1^2 - \sum_{all \mu} \frac{Z_\mu}{r_{\mu 1}} \quad (2.9)$$

H_{ii} is the core integral, representing the kinetic energy of a single electron and its potential energy of attraction to all nuclei in the molecule. In other words, it corresponds to the energy of a one-electron system under the hypothetical assumption that all other electrons are absent. J_{ij} is the Coulomb integral, that expresses the electrostatic repulsion between one electron located in orbital i and another located in orbital j :

$$J_{ij} = \int \psi_i^*(1) \psi_i(1) \frac{1}{r_{12}} \psi_j^*(2) \psi_j(2) dv_1 dv_2 \quad (2.10)$$

The term inside the integral is the potential energy of electrostatic repulsion between one electron in dv_1 and another electron in dv_2 . K_{ij} is the exchange integral, and its function is

that of accounting for the fact that same-spin electrons tend to avoid each other due to Pauli repulsion:

$$K_{ij} = \int \psi_i^*(1)\psi_j^*(2) \frac{1}{r_{12}} \psi_i(2)\psi_j(1) dv_1 dv_2 \quad (2.11)$$

This creates Fermi holes that effectively reduce the Coulomb repulsion, highlighted by the opposite signs of the Coulomb and exchange integrals in Equation 2.7.

Equation 2.7 is differentiated with respect to the ψ_i to find those that minimize the energy. This returns the Hartree-Fock equations, whose compact form is found below:

$$\begin{aligned} \hat{F}\psi_1(1) &= \epsilon_1\psi_1(1) \\ \hat{F}\psi_2(1) &= \epsilon_2\psi_2(1) \\ \hat{F}\psi_3(1) &= \epsilon_3\psi_3(1) \\ &\vdots \\ \hat{F}\psi_n(1) &= \epsilon_n\psi_n(1) \end{aligned} \quad (2.12)$$

Here, $\hat{F}$ denotes the Fock operator, i.e., the effective one-electron Hamiltonian, and $\epsilon_1 \dots \epsilon_n$ represent the orbital energies associated with the molecular orbitals $\psi_1(1) \dots \psi_n(1)$. The 1 in parentheses indicates that each occupied spinorbital contributes one electron to the system. The Hartree-Fock equations constitute a pseudo-eigenvalue problem, since the operator $\hat{F}$ depends explicitly on the set of orbitals ψ_i on which it acts, but they can be nevertheless be intended as one-electron Schrödinger equations.

In their original form, the Hartree-Fock equations are mathematically intractable due to the complexity of the molecular orbital expressions. Independently, Roothaan and Hall recognized that both the construction of initial guesses for the molecular orbitals and the practical implementation of the calculations could be significantly simplified by expanding the molecular orbitals as linear combinations of predefined basis functions, as shown below:

$$\psi_1 = c_{11}\phi_1 + c_{21}\phi_2 + c_{31}\phi_3 + \dots + c_{m1}\phi_m \quad (2.13)$$

$$\psi_2 = c_{12}\phi_1 + c_{22}\phi_2 + c_{32}\phi_3 + \dots + c_{m2}\phi_m \quad (2.14)$$

$$\psi_3 = c_{13}\phi_1 + c_{23}\phi_2 + c_{33}\phi_3 + \dots + c_{m3}\phi_m \quad (2.15)$$

$$\vdots \quad (2.16)$$

$$\psi_m = c_{1m}\phi_1 + c_{2m}\phi_2 + c_{3m}\phi_3 + \dots + c_{mm}\phi_m \quad (2.17)$$

This formulation leads to the Roothaan-Hall equations, whose compact matrix representation is given below.

$$\mathbf{FC} = \mathbf{SC}\epsilon \quad (2.18)$$

Where $\mathbf{F}$ is the Fock matrix, $\mathbf{S}$ is the overlap matrix whose elements are the overlap integrals $S_{ij} = \int \phi_i \phi_j dv$, $\mathbf{C}$ is the matrix of coefficients of the basis functions and ϵ is the diagonal matrix containing the energies of the molecular orbitals. Modern ab initio methods self-consistently solve the Roothaan-Hall equations by diagonalizing the Fock matrix and finding the basis functions coefficients and energies of the molecular orbitals. To kickstart the SCF cycle, the initial guess of the wavefunction is typically obtained by superposition of the atomic wavefunctions. Different types of basis functions have been employed in quantum chemical methods, including Slater-type orbitals (STOs) and Gaussian-type orbitals (GTOs). Although STOs more closely resemble the exact hydrogenic solutions, Gaussian functions are generally preferred because they are more easily tractable. In periodic electronic structure calculations, plane-wave basis sets are commonly used due to their natural compatibility with periodic boundary conditions.

HF methods suffer from the incomplete treatment of correlation of electrons' motion. By introducing the wavefunction in the form of a Slater determinant, HF methods account for Pauli repulsion, but still fail to faithfully reproduce Coulombic repulsion. This, in fact, is treated as the repulsion between the one-electron wavefunction and the smeared-out electric field generated by all the other one-electron wavefunctions, which does not account for instantaneous repulsion. This concept can be illustrated by analogy. Imagine walking down a crowded street in which the motion of pedestrians is described only by an average flow field. In such a scenario, we would incur in collisions that could be avoided if the motion of each individual were treated explicitly, and we were able to adjust our direction accordingly. Similarly, the mean-field treatment of electron-electron repulsion in HF theory neglects instantaneous correlations between electrons, leading to an overestimation of the total energy. To account for this missing correlation energy, numerous post-HF methods have been developed that incorporate electron correlation in a systematic manner. Although these approaches are computationally demanding, they are generally regarded as the benchmark for accuracy in computational chemistry. A detailed discussion of these methods, however, lies beyond the scope of this thesis. In the next section we will instead discuss a fundamentally different approach to quantum chemical calculations, namely Density Functional Theory (DFT). Due to its relatively high accuracy against moderate computational cost, DFT is nowadays regarded as the workhorse of computational chemistry.

2.1.3. Density Functional Theory

DFT is a quantum mechanical approach that seeks to derive the properties of a system not from its wavefunction, as HF and post-HF methods, but rather from the electron density ρ . There are three main reasons for which DFT represents an attractive alternative to wavefunction-based methods: ρ is experimentally measurable, intuitively more understandable and, importantly, easier to treat from a mathematical perspective. Unlike the

wavefunction that depends on $4n$ variables (position and spin) where n is the number of electrons, in fact, ρ is a function of just the three cartesian coordinates x, y and z regardless of the size of the system.

The forefathers of modern DFT are Thomas and Fermi, that in the 20s developed a model that described atoms as composed of a positively charged nucleus surrounded by an homogeneous electron cloud. A further contribution to this approach came from Dirac, that showed how electron exchange could be included in the Thomas-Fermi model in a similar fashion as the Hartree-Fock theory improved the Hartree model. Modern DFT methods, however, rely on the so-called Kohn-Sham approach.[126] This lays its foundation on the two Hohenberg-Kohn theorems first published in 1964,[127] that state the following:

1. All the properties of a molecule in a ground electronic state are determined by the ground state electron density function, i.e. they are a *functional* of $\rho_0(x, y, z)$.
2. Any trial electron density function will give an energy equal or higher than the true ground state energy.

The first is an existence theorem, that states that in principle a functional exist that applied to ρ_0 can give us the property of interest (in most cases, the energy), while the second states that a variational approach may be used to calculate ρ_0 and the energy of the system.

The core idea of Kohn-Sham DFT is to express the energy of the system as a sum of terms that can be calculated exactly, plus an additional term, ideally small, where all the other factors are included. The ground state electronic energy is calculated according to the following expression:

$$E_0 = \langle T[\rho_0] \rangle + \langle V_{Ne}[\rho_0] \rangle + \langle V_{ee}[\rho_0] \rangle \quad (2.19)$$

The terms on the right-hand side of the above equation are, from left to right, the electronic kinetic energy, the electrons-nuclei and electron-electron potential energies. The second term can be calculated exactly as:

$$\langle V_{Ne}[\rho_0] \rangle = - \sum_{\text{nuclei } A} Z_A \int \frac{\rho_0(\mathbf{r}_1)}{r_{1A}} d\mathbf{r}_1 \quad (2.20)$$

To calculate the other terms, it useful to resort to a fictitious reference system of non-interacting electrons whose ground state electron density is exactly the same as that of the real system. By using this expedient, the first and third terms can be written as:

$$\langle T[\rho_0] \rangle = \langle T[\rho_0] \rangle_{ref} + \Delta \langle T[\rho_0] \rangle \quad (2.21)$$

$$\langle V_{ee}[\rho_0] \rangle = \langle V_{ee}[\rho_0] \rangle_{ref} + \Delta \langle V_{ee}[\rho_0] \rangle \quad (2.22)$$

The electron-electron repulsion potential energy of the non-interacting reference system can be written as:

$$\langle V_{ee}[\rho_0] \rangle_{ref} = -\frac{1}{2} \iint \frac{\rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.23)$$

This is the classical charge-cloud repulsion term. It is worth noting that this expression implies that each electron somewhat repels itself, since it is smeared out over the cloud from which it feels the repulsion. This *self-interaction error* is a known shortcoming of DFT. As it will be shown in Section 2.1.3.2, one way to mitigate this error is implementing the Hubbard correction.

The kinetic energy term of the non-interacting system is the expectation value of the sum of the one-electron kinetic energy, that can be written as:

$$\langle T[\rho_0] \rangle_{ref} = -\frac{1}{2} \sum_{i=1}^{2n} \langle \psi_i^{KS}(1) | \nabla_1^2 | \psi_i^{KS}(1) \rangle \quad (2.24)$$

Where $\psi_i^{KS}(1)$ are the Kohn-Sham spin orbitals. Finally, by collecting the unknown terms in the so-called exchange-correlation energy:

$$E_{XC}[\rho_0] = \Delta \langle V_{ee}[\rho_0] \rangle + \Delta \langle T[\rho_0] \rangle \quad (2.25)$$

And the ground state electronic energy can be expressed as:

$$E_0 = - \sum_{nuclei A} Z_A \int \frac{\rho_0(r_1)}{r_{1A}} dr_1 - \frac{1}{2} \sum_{i=1}^{2n} \langle \psi_i^{KS}(1) | \nabla_1^2 | \psi_i^{KS}(1) \rangle + \frac{1}{2} \iint \frac{\rho_0(r_1) \rho_0(r_2)}{r_{12}} dr_1 dr_2 + E_{XC}[\rho_0] \quad (2.26)$$

We note that the introduction of the Kohn-Sham orbitals is not a rigid theoretical requirement in DFT, but simply a convenient way to make Equation 2.26 approachable from a mathematical perspective. The Kohn-Sham orbitals are linked to the electron density via:

$$\rho_0 = \sum_{i=1}^{2n} |\psi_i^{KS}(1)|^2 \quad (2.27)$$

Similarly to the Hartree-Fock procedure, the ground state energy can be minimized with respect to the Kohn-Sham orbitals to yield the Kohn-Sham equations:

$$\left[-\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{XC}(1) \right] \psi_i^{KS}(1) = \epsilon_i^{KS} \psi_i^{KS}(1) \quad (2.28)$$

Additionally, the exchange-correlation potential in Equation 2.28 is given by differentiation of the exchange-correlation energy with respect to the electron density (or, in the actual computational procedure, with respect to the Kohn-Sham orbitals):

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \quad (2.29)$$

The Kohn-Sham equations in compact form become:

$$\hat{h}^{KS}(1)\psi_i^{KS}(1) = \epsilon_i^{KS}\psi_i^{KS}(1) \quad (2.30)$$

Where $\hat{h}^{KS}(1)$ is the Kohn-Sham operator. As in Hartree-Fock theory, the Kohn-Sham orbitals are expanded as a linear combination of basis function and the DFT analogous of the Roothan-Hall equations is obtained.

In principle, Equation 2.26 would be exact if the exact form of the exchange-correlation functional was known. This is, of course, not the case, and the main challenge in DFT is to improve the expression of E_{XC} , even though there is no systematic way to do that. Increasing the complexity (and ideally the accuracy) of E_{XC} has over time spawned a variety of different flavors of Kohn-Sham DFT, that are frequently metaphorically described as the rungs of a (Jacob's) ladder, visually depicted in Figure 2.1, that will eventually take us to heaven, or in other words to chemical accuracy. It is worth noting that, within each rung, several different XC functionals have been proposed.

At the first rung, local density approximation (LDA) functionals are found, which assume that at each point in a molecular system, the exchange–correlation energy density is equal to that of a homogeneous electron gas possessing the same local electron density. The generalized gradient approximation (GGA) functionals are located one rung above. These are often referred to as semilocal XC functionals because, in addition to the point-value of the electron density, they also include its gradient. GGA functionals are nowadays widely used in DFT studies and especially in catalysis-related applications. Some of the most common GGA functionals are the Perdew-Burke-Ernzerhof (PBE)[128], the Perdew-Wang (PW) 91 [129] and the revised (R)PBE [130]. Above the GGA level of theory we find Meta-GGA functionals, that in their expression figure both the point-value, the gradient and the second derivative of the electron density. Further above, we find hybrid GGA and meta-GGA functionals, that express the XC energy as a weighted sum of the DFT XC and HF exchange energy. Adding a percentage of exact HF exchange to the DFT treatment leads to substantial improvements, and in particular mitigates the above-mentioned self-interaction error inherent to DFT. The most common Hybrid functionals are B3LYP[131] and PBE0 [132]. The highest rung of Jacob's ladder is occupied by the fully non-local XC functionals. While local and semilocal functionals take into account the electron density point value and the infinitesimal region around the point value, respectively, non local functionals are expected to treat the effects that occur at finite distances from the considered point, that are Pauli repulsion and electron correlation. Unlike lower rungs in the ladder, these type of functionals do not have a common, prescribed form, and different

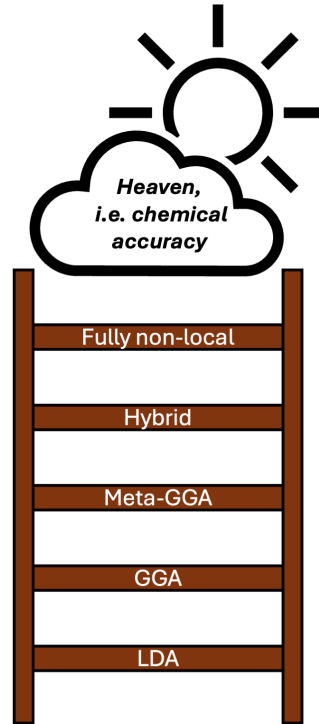


Figure 2.1.: Graphical depiction of Jacob's ladder, or the different rungs of accuracy of DFT exchange-correlation functionals.

formulations use different strategies to tackle the exchange-correlation problem. Double-hybrid functionals such as B2PLYP[133] belong to this category, as they combine a fraction of exact Hartree–Fock exchange with a perturbative second-order Møller–Plesset (MP2) correlation contribution evaluated on top of the Kohn–Sham orbitals. Another prominent example of non-local XC functionals approach is the random phase approximation (RPA), that is based on the adiabatic-connection fluctuation–dissipation theorem.[134]

Within this thesis, we will exclusively employ a rung 2 GGA functional, namely the Bayesian Error Estimation Functional with van der Waals correlation (BEEF-vdW),[135] that will be discussed more in detail in the next section.

2.1.3.1. The BEEF-vdW Exchange-Correlation Functional

The BEEF-vdW XC energy is constructed as sum of an exchange and a correlation part. The correlation part includes a weighted sum of the PBE and LDA correlation energies and the non-local correlation energy as implemented in the vdW-DF2 functional, that accounts for the dispersion effects associated to van der Waals interactions.[136] The general form of the exchange energy of GGA functionals is the following:

$$E_x^{\text{GGA}}[\rho, \nabla\rho] = \int \varepsilon_x^{\text{UEG}}(\rho) F_x[s(\rho, \nabla\rho)] \, d\mathbf{r} \quad (2.31)$$

Where $\epsilon_x^{\text{UEG}}(\rho)$ is the energy density of the uniform electron gas, while $F_x[s(\rho, \nabla\rho)]$ is the exchange enhancement factor that is function of the adimensional electron density gradient s . In the BEEF-vdW functional, the exchange enhancement factor is expanded as a sum of Legendre polynomials ultimately yielding:

$$E_x^{\text{GGA}}[n, \nabla n] = \sum_m a_m E_{x,m}^{\text{GGA}}[n, \nabla n] \quad (2.32)$$

Where a_m are expansion coefficients and $E_{x,m}^{\text{GGA}}[n, \nabla n]$ is the exchange energy corresponding to the Legendre basis function B_m . Hence, the total of XC energy is given by:

$$E_{XC} = \sum_{m=0}^{M_x-1} a_m E_m^{\text{GGA-x}} + \alpha_c E^{\text{LDA-c}} + (1 - \alpha_c) E^{\text{PBE-c}} + E^{\text{nl-c}} \quad (2.33)$$

Where $E^{\text{LDA-c}}$, $E^{\text{PBE-c}}$ and $E^{\text{nl-c}}$ are the LDA, PBE and non-local correlation energies, respectively, while α_c is the correlation parameter comprised between 0 and 1. In the formulation of the BEEF-vdW functional, the 30 expansion coefficients a_m plus α_c are obtained from the best fit of different datasets, obtained experimentally or from high-level of theory *ab initio* calculations, that include molecular formation energies, reaction energies, noncovalent interactions, solid state properties and chemisorption on solid surfaces. Hence, the BEEF-vdW functional is semi-empirical in nature and could even be regarded as an early machine-learning inspired GGA functional.

A unique feature of BEEF-vdW with respect to the other XC functionals is that it can provide an error estimation based on Bayesian statistic.[137] This consists in applying perturbations to the model parameters based on a predefined probability distribution to obtain an ensemble of hypothetical GGA functionals. A representation of the Bayesian ensemble of XC functionals around BEEF-vdW is shown in Figure 2.2.

The energy of the system under study can then be recalculated with each functional of the ensemble, taking as input the electron density calculated self-consistently from the optimal BEEF-vdW XC. This procedure generates an energy distribution whose root-mean square deviation (RMSD) indicates the accuracy of the calculation. In other words, the accuracy is given in terms of the energy range that could be obtained by using any plausible GGA functional. We will make use of this special feature of the BEEF-vdW functional in Chapter 3, where we will estimate the accuracy of our calculations of CO dissociation barriers on different fcc-Co sites. Finally, we note that the BEEF-vdW functional exhibits an optimal tradeoff between the accuracies of CO adsorption and surface energies calculations,[135] which is critical for our study as both quantities will be employed to build models of Co NPs in a CO gas phase in Chapter 4.

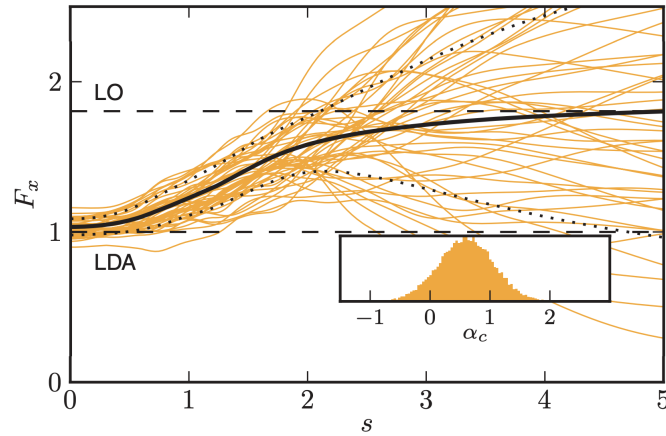


Figure 2.2.: The relation between the enhancement factor F_x and the adimensional electron density gradient s for the different GGA functionals of the BEEF-vdW ensemble. The solid black line indicates the optimal BEEF-vdW functional, while the lower and upper dashed lines indicate the LDA and Lieb-Oxford limits, respectively. The inset shows a histogram of the distribution of correlation parameters in an ensemble containing 20 000 samples. Reprinted with permission from Reference [135].

2.1.3.2. Hubbard Correction

A known shortcoming of DFT is its failure to accurately describe so-called strongly-correlated systems, that are compounds where electron correlation significantly affects the electronic structure. This difficulty arises from the approximate treatment of electron correlation in DFT, and especially from the self-interaction error discussed in Section 2.1.3, which causes an artificial coulombic repulsion that becomes particularly problematic for electrons in spatially confined d and f orbitals. As a result, d and f electrons tend to wrongly over-delocalize, notoriously leading to drastic underestimation of band-gaps and often to predictions of metallic behavior for compounds that are experimentally insulators.[138] A paradigmatic example of these compounds are Mott insulators,[139, 140] for which DFT fails to reproduce the bandgap originating from the strong repulsion associated to double occupancy of localized orbitals. Furthermore, the incorrect description of the electronic structure of these compounds also leads to poor predictions of reaction energies and barriers.

Notably, the exact exchange treatment of HF and post-HF methods cancels the self-interaction error. Hence, by including a percentage of HF exchange, hybrid DFT methods lead to substantial improvements in the predictions in comparison to local and semilocal functionals,[141] but are also significantly more computationally demanding. An inexpensive computational approach to mitigate this issue is the Hubbard method, also indicated as the DFT+U formulation. The advantage of DFT+U is that it can be applied directly to the LDA or GGA Hamiltonians, which is done by adding to the standard DFT energy an intra-atomic on-site repulsion term acting on d and f KS orbitals and subtracting a term that avoids double-counting:

$$E^{DFT+U}[n, \hat{n}] = E^{DFT}[n] + E_U[\hat{n}] - E_{dc}[\hat{n}] \quad (2.34)$$

Where $E^{DFT+U}[n, \hat{n}]$ is the DFT+U energy, $E^{DFT}[n]$ is the plain DFT energy, $E_U[\hat{n}]$ is the Hubbard energy correction term, $E_{dc}[\hat{n}]$ is the double-counting term, n is the electron density and $\hat{n}$ is the on-site occupancy matrix of localized d and f orbitals. The elements of the on-site occupancy matrices are obtained via projection of the occupied KS orbitals onto the atomic-orbital localized basis sets. Among the different formulations of the Hubbard correction that have been proposed, in this thesis we will employ the simplified rotationally invariant (under rotation of the atomic orbital basis) approach developed by Dudarev et al.[142], that expresses the DFT+U energy as:

$$E^{DFT+U} = E^{DFT} + \frac{U-J}{2} \sum_{\sigma} \left[\left(\sum_{m_1} \hat{n}_{m_1 m_1}^{\sigma} \right) - \left(\sum_{m_1, m_2} \hat{n}_{m_1 m_2}^{\sigma} \hat{n}_{m_2 m_1}^{\sigma} \right) \right] \quad (2.35)$$

Where U and J are the effective on-site Coulomb and exchange interactions, respectively, while $\hat{n}_{m_1 m_1}^{\sigma}$ and $\hat{n}_{m_1 m_2}^{\sigma}$ are the diagonal and off-diagonal elements of the matrix in the localized d and f orbital subspace. In practice, this approach introduces an energy penalty for fractional orbital occupancy which favors electron localization. In this formulation, the individual values of U and J are irrelevant and only their difference (often indicated as U_{eff}) determines the magnitude of the on-site correction.

The appropriate value of U_{eff} for the system under study, however, is not known *a priori*, and its choice is often complicated by the fact that no single U_{eff} yields satisfactory predictions of all the properties of interest. Nonetheless, there has been significant effort to develop strategies aimed at predicting U_{eff} from first principles,[143–145] of which the most popular is probably the linear-response method elaborated by Cococcioni and De Gironcoli.[146] According to this methodology, U_{eff} is computed self-consistently as the curvature of the DFT total energy with respect to the occupation of a localized subspace. It is defined so as to cancel the spurious deviation from piecewise linearity of the approximate DFT functional between integer occupations of that localized orbital. This procedure, however, is rather computationally tedious and might still yield unsatisfactory agreement with experiments, which causes most studies to actually determine U_{eff} semi-empirically, i.e. by calibrating its value to reproduce the property/ies of interest. While the majority of works rely on the experimental bandgap, for catalysis applications such as the one discussed in this thesis the correct description of reaction energies is a more crucial aspect to consider. For this reason, in Chapters 3 and 5 we will calibrate the U_{eff} applied to the $3d$ orbitals of Co^{2+} and Mn^{2-4+} to match the experimental oxidation energies of Co^0 to CoO and of MnO to Mn_3O_4 , Mn_2O_3 and MnO_2 , respectively.

2.2. Machine-Learning Interatomic Potentials

A multitude of physical phenomena occur on length and time scales that are untreatable with DFT. DFT calculations, in fact, are limited to systems of a few hundreds of atoms, while *ab initio* molecular dynamics (aiMD) simulations can run at most for dozens of picoseconds. On the other hand, physics-based potentials employed in classical MD simulations can

handle significantly larger systems (thousands of atoms) and longer simulation times (nanoseconds), but their heavily constrained form, mostly based on physics intuition, yields drastically less accurate results in comparison to *ab initio* methods.

The advent in recent years of Machine-Learning Interatomic Potentials (MLIPs) holds the potential to revolutionize computational chemistry, as these methods can yield near *ab initio* accuracy at the cost of classical physics-based potential. The fundamental idea of MLIPs is to construct an approximate Potential Energy Surface (PES) by training a model on a dataset of chemical structures whose properties were previously evaluated with DFT, and to then infer the properties of new structures via interpolation. In Figure 2.3 we show the typical workflow to construct an MLIP, that is exemplified in three main steps. The starting point is the construction of the reference DFT dataset, that should ideally be large and diverse to guarantee accurate results. To date, however, there is no standardized way to carry out this task. While random sampling of structures e.g. from an aiMD trajectory can be an effective strategy, it is certainly not the most efficient. A popular technique that is commonly adopted is active learning, that consists of invoking an *ab initio* calculation only when a structure falls outside the previously sampled domain. To evaluate whether a structure is out-of-domain, MLIPs architectures make use of uncertainty estimation techniques such as the Bayesian linear regression. Once the dataset is built, its structures are translated into a numerical representation, operation often indicated as atomic environment featurization (AEFs). Lastly, regression of the extracted features, also denoted as embeddings, against the DFT labels allows to obtain a smooth PES where new data points can be interpolated.

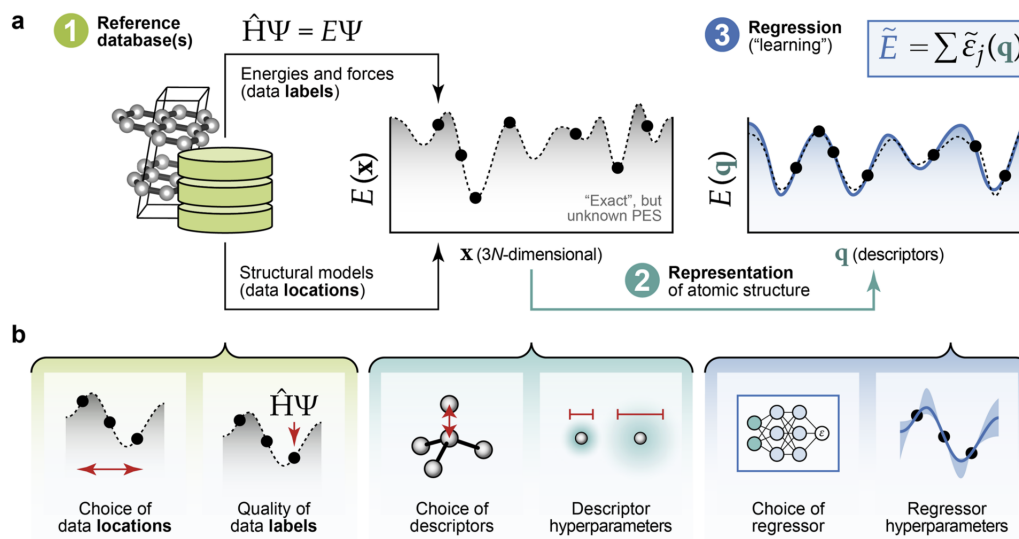


Figure 2.3.: Visual depiction of the typical procedure to construct an MLIP. Reprinted with permission from Ref. [147].

Due to the rapid developments in the field, a rigid classification of MLIP architectures remains challenging. Nevertheless, one of the main diverging points across different models is whether the AEF is explicit or implicit.[148] The core difference between the two

approaches is that while explicit AEF MLIPs describe the target atom environment via a set of predefined basis functions, in implicit AEF MLIPs these are learned. In the latter approach, the database structures are converted into graphs, where atoms are represented as nodes and bonds as edges. The graphs are then subject to a Graph Neural Network (GNNs) regression, that iteratively updates the different atom embeddings and maps them against the energy labels. In fact, the second and third steps depicted in Figure 2.3 occur simultaneously in implicit AEF MLIPs and cannot be decoupled. The main advantage of implicit AEF is that it yields more versatile MLIPs that can treat systems with many (>5) elements more easily with respect to those built via explicit AEF, but at the cost of lower computational efficiency.

Since they are typically constructed *ad-hoc* for a specific application, conventional MLIPs cover a rather limited spectrum of chemical environments. Recently, however, so-called universal (u)MLIPs have emerged as a result of training on large datasets containing millions of structures covering most of the periodic table. What makes uMLIPs particularly attractive is that they are ready-made potentials that can treat an enormous range of different compounds while maintaining a high-level stability adequate for MD simulations. On the other hand, their accuracy has not been thoroughly validated for most systems and may be unsatisfactory when they are employed in a new application. Therefore, they are often used as a robust basis that is further fine-tuned on a smaller dataset targeting a specific chemical environment. Some of the most popular uMLIPs are M3GNet,[149] MACE-MP0[150] and CHGNet[151]. In the following, we will briefly describe the architecture of CHGNet, that is the uMLIP employed in this thesis. CHGNet is trained on the MPtrj dataset, and employs an implicit AEF architecture that makes use of an atom graph representation to extract pairwise features and an auxiliary bond graph to encode angles. At the start of the training procedure, the environment of each atom is featurized in three vectors encoding atomic numbers, bonds and angles considering only its immediate vicinity, that in CHGNet is defined with a radial cutoff of 5 Å. The features are then iteratively updated in a message-passing graph convolution, during which, at each layer, information from the next coordination shell are included in the atomic features. Hence, at the first convolution layer, the atomic features include the target atom environment and those of the neighboring atoms, at the second layer they include the target atom environment, those of the neighboring atoms and those of the next-neighboring atoms and so on. Since CHGNet employs four convolution layers, it is capable to featurize long-range interactions upto distances of 20 Å at a moderate computational cost. Throughout training, the parameters of the GNN, including the weights governing the embedding updates and the final energy readout, are optimized to minimize the loss with respect to the target properties in the dataset. A unique feature of CHGNet with respect to other MLIPs is that, in addition to energies, forces and (in case periodic structures are considered) stress, it can be trained on the DFT-calculated magnetic moments, from which atoms valency can be inferred.

In Chapter 5, we will fine-tune the original CHGNet on a DFT dataset of $\text{Mn}_x\text{O}_y\text{H}_z$ structures on different Co facets and will obtain near-DFT accuracy. We will then use the fine-tuned potential as internal calculator in a genetic algorithm (GA) to optimize Mn structures on Co NPs. Additionally, the predictions of the magnetic moments will be used to derive the charge of Mn in the identified global minima (GM) structures.

2.3. Genetic Algorithm

Having a correct representation of the active sites in a catalyst is arguably one of the most critical points for DFT calculations. In this regard, constructing the models by simply relying on chemical intuition might be misleading due to the complexity of the PES of most real systems. To overcome this, several computational techniques indicated as Global Optimization (GO) methods have been elaborated to carry out an automated, comprehensive and unbiased probe of the PES, that ultimately leads to a more realistic active site representation. One of the most popular GO methods is the Genetic Algorithm (GA), that owes its name to the fact that it employs principles resembling Darwinian natural selection to yield low-energy candidates. In particular, starting from a pool of randomly generated structures, the GA produces offspring by combining the features of the *fittest* candidates, that hence are allowed to propagate their genetic makeup. Offspring are then included in the population pool that is iteratively updated and may be employed in a new pairing procedure. In the following, we will describe the algorithm workflow in the implementation by Vilhelmsen and Hammer,[152, 153] that is the one employed in Chapter 5 of this thesis.

The initial population is usually constructed by randomly placing the atoms of the user-defined optimization cluster in a confined volume. For heterogeneous catalysis application, the optimization cluster is typically placed on a solid surface that can be allowed to relax. It is important that the starting population pool is large and diverse enough so that the best combination of the available genes can yield energetically favorable candidates. Once the initial structures have been relaxed, two candidates are chosen for the pairing procedure based on a pairing probability P_i given by:

$$P_i = F_i \cdot U_i \quad (2.36)$$

Where F_i and U_i are the fitness and uniqueness of the i th candidate that are defined as follows:

$$F_i = \frac{1}{2} [1 - \tanh(2\rho_i - 1)] \quad (2.37)$$

$$U_i = \frac{1}{\sqrt{1 + n_i}} \cdot \frac{1}{\sqrt{1 + m_i}} \quad (2.38)$$

And

$$\rho_i = \frac{E_i - E_{min}}{E_{max} - E_{min}}. \quad (2.39)$$

Where n_i is the number of times candidate i has participated in a pairing procedure and m_i is the number of candidates which are structurally similar to the i th candidate but not included in the population pool, while E_{max} and E_{min} are the energies of the global

maximum and minimum in the population pool, respectively. It is worth mentioning that while F_i determines the algorithm drive towards more energetically favorable candidates, U_i ensures that enough diversity is maintained so that the algorithm is not trapped in local minima basins. The second factor has been demonstrated to be even more important than the first to carry out a successful run.[152] The strategy used to combine two parent structures plays a decisive role in the performance of a GA. A commonly adopted recombination scheme is the cut-and-splice method, graphically depicted in Figure 2.4.

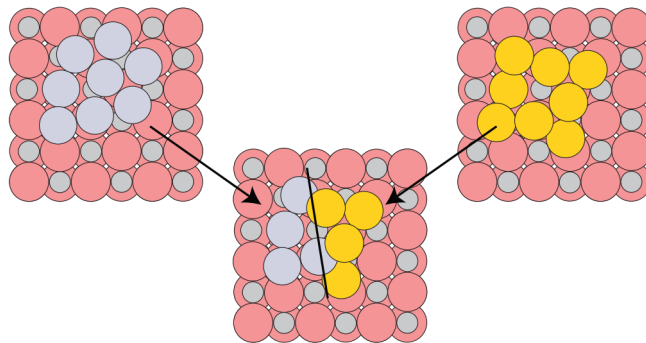


Figure 2.4.: Visual depiction of the cut-and-splice offspring generation technique. Reprinted with permission from Ref. [152].

In this procedure, the parent structures are partitioned by a randomly oriented surface that intersects their shared center of mass, and complementary fragments from each parent are merged to construct a new candidate. In its simplest form, the partition is defined by a plane, although more elaborate geometries, such as spherical dividing surfaces,[154] have also been implemented successfully.

Once the offspring is relaxed, it is added to the population pool if it is more stable than the least stable preexisting candidate and also structurally unique. The candidate is considered structurally unique if it satisfies at least one of the two following conditions:

$$\frac{\sum_k |D_i(k) - D_j(k)|}{\frac{1}{2}(\sum_k |D_i(k) + D_j(k)|)} > \delta_{rel} \quad (2.40)$$

$$\max_k (|D_i(k) - D_j(k)|) > d_{max} \quad (2.41)$$

Where eq. 2.40 checks that the cumulative interatomic distances between the offspring and any other candidate in the population pool are larger than δ_{rel} , while eq. 2.41 compares their maximum interatomic distances against d_{max} .

Before relaxation, the offspring might undergo a mutation with a certain user-defined probability, whose function is to introduce genetic features that were not initially present in the population pool and hence to broaden the probing of the PES. Different mutation types have been previously proposed, among which the most common are:

- Rattle: a percentage of the atoms in the structure are randomly displaced along a random direction;
- Twist: for supported systems, the entire cluster is rotated by a random angle around the surface normal of the support;
- Permutation: the chemical identities of a portion of the atoms are randomly reassigned, enabling the exploration of new compositional arrangements while leaving the atomic positions unchanged;
- Mirror: the structure is divided by a randomly oriented plane, and one of the resulting fragments is reflected.

GA algorithms have been employed to study a variety of different systems, including optimization of bimetallic NPs[154] as well as metal clusters supported on zeolites[155, 156] and on oxide surfaces [157]. Furthermore, recent developments have improved the standard GA formulation to consider a grand canonical treatment of the PES.[158] In Chapter 5, we will present for the first time a GA approach to optimize structures adsorbed on metal NPs models. In particular, we will employ a GA to optimize Mn oxidic clusters at realistic loadings on both fcc and hcp Co NPs. Importantly, the exploration of such large systems was enabled by employing the fine-tuned CHGNet uMLIP as internal calculator.

2.4. Thermodynamic Frameworks

The partition function is a core concept of statistical thermodynamics that serves as a basis to construct all the state functions. Given a system at fixed composition, volume and temperature (i.e. a canonical ensemble) with i available microstates each with energy ϵ_i , the partition function Q is given by:

$$Q = \sum_i e^{-\frac{\epsilon_i}{k_b T}} \quad (2.42)$$

And the probability of occurrence of the i_{th} microstate is given by:

$$p_i = \frac{e^{-\frac{\epsilon_i}{k_b T}}}{Q} \quad (2.43)$$

It can be shown that the internal energy U and entropy S , from which all the other state functions can be obtained, are linked to the partition function via the following equations:

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \quad (2.44)$$

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q \quad (2.45)$$

The global partition function can be written as the products of the partition functions of the individual degrees of freedom, that for a molecular system are:

$$q_{tot} = q_{trans} \cdot q_{rot} \cdot q_{vib} \cdot q_{elec} \quad (2.46)$$

where q_{trans} , q_{rot} , q_{vib} and q_{elec} are the translational, rotational, vibrational and electronic partition functions. Similarly, the entropy of the system may be written as:

$$S_{tot} = S_{trans} + S_{rot} + S_{vib} + S_{elec} \quad (2.47)$$

The translational partition functions for a molecule confined in a three-dimensional space of volume V , the rotational partition function for a nonlinear molecule and the vibrational partition functions are given by:

$$q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V, \quad (2.48)$$

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \sqrt{I_x I_y I_z}, \quad (2.49)$$

$$q_{vib} = \prod_{i=1}^{3N-6} \frac{1}{1 - \exp\left(-\frac{\hbar\omega_i}{k_B T}\right)}. \quad (2.50)$$

When considering only the electronic ground state, q_{elec} is simply equal to 1. The corresponding entropic contributions are:

$$S_{trans} = k_B \left[\ln \left(\frac{k_B T}{P} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right) + \frac{5}{2} \right], \quad (2.51)$$

$$S_{\text{rot}} = \begin{cases} k_B \left[1 + \ln \left(\frac{8\pi^2 I k_B T}{\sigma h^2} \right) \right], & \text{linear molecules} \\ \frac{1}{2} k_B \left[3 + \ln \left(\frac{\pi}{\sqrt{\sigma}} \left(\frac{8\pi^2 k_B T}{h^2} \right)^3 I_x I_y I_z \right) \right], & \text{nonlinear molecules} \end{cases} \quad (2.52)$$

$$S_{\text{vib}} = k_B \sum_i \left[\frac{\hbar \omega_i}{k_B T (e^{\hbar \omega_i / k_B T} - 1)} - \ln \left(1 - e^{-\hbar \omega_i / k_B T} \right) \right] \quad (2.53)$$

$$S_{\text{elec}} = k_B \ln [2 \times (\text{total spin}) + 1] \quad (2.54)$$

Where σ is the molecule symmetry number, $I_{x,y,z}$ and I are the moment of inertia in the three cartesian coordinates and the degenerate moment of inertia for non-linear and linear molecules, respectively and ω_i is the frequency of the i_{th} vibrational mode.

Electronic energies obtained from DFT calculations have little practical use by themselves, since we are usually more interested in thermodynamic state functions that can be related to the real-world driving forces of the phenomena of interest. To overcome this limitation, the Gibbs free energy is typically retrieved by applying thermal corrections to the DFT energy. The nature of these corrections, however, depends on the thermodynamic framework employed to describe the system under scrutiny. In the following, we will present the two thermodynamic schemes employed throughout this thesis, i.e. the ideal gas and harmonic oscillator approximations.

Ideal gas approximation. Small gas-phase molecules such as CO, H₂ and H₂O are usually described within the ideal gas approximation. The Gibbs free energy $G(T, P)$ is given by:

$$G(T, P) = H(T) - TS(T, P) \quad (2.55)$$

it is worth noting that, for an ideal gas, the enthalpy is not a function of pressure. Having DFT calculations as a starting point, it is most convenient to retrieve $H(T)$ via extrapolation from 0 K to the T of interest:

$$H(T) = E_{\text{elec}} + E_{\text{ZPE}} + \int_0^T C_P dT \quad (2.56)$$

Where E_{elec} is the electronic energy obtained from DFT, E_{ZPE} is the zero-point energy (ZPE) and C_P is the constant-pressure heat capacity. The ZPE is a quantum-mechanical effect that arises from the residual nuclear motion that persists even at 0 K. Nuclei in a molecule can be seen as harmonic oscillators, for which the solutions of the Schrödinger equation yield energy levels of the form $E_n = (n + \frac{1}{2})\hbar\omega$, where n is the principal quantum number. From this expression, it becomes apparent that the ground-state energy ($n = 0$) is not zero but equal to $E_{\text{ZPE}} = \frac{1}{2}\hbar\omega$. Hence, the ZPE for a molecular system with i vibrational modes is:

$$E_{ZPE} = \sum_i \frac{1}{2} \hbar \omega_i \quad (2.57)$$

On the other hand, the adiabatic and the isochoric heat capacities of an ideal gas are related via:

$$C_P = k_b T + C_V = k_b T + C_{V,\text{trans}} + C_{V,\text{rot}} + C_{V,\text{elec}} + C_{V,\text{vib}} \quad (2.58)$$

The translational heat capacity is $\frac{3}{2}k_b$ while the rotational heat capacity is 0 for a monatomic species, k_b for a linear molecule, and $\frac{3}{2}k_b$ for a nonlinear molecule. The electronic component of the heat capacity is usually neglected. The integral of the vibrational heat capacity is given by:

$$\int_0^T C_V dT = \sum_i \frac{\hbar \omega_i}{e^{\frac{\hbar \omega_i}{k_b T}} - 1} \quad (2.59)$$

Finally, the ideal gas entropy can be calculated as:

$$S(T, P) = S(T, P^0) - k_b \ln \frac{P}{P^0} = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}} - k_b \ln \frac{P}{P^0} \quad (2.60)$$

Where the expressions for the individual components of the entropy are those presented in Equations 2.51, 2.52, 2.53 and 2.54.

Harmonic oscillator approximation. Small, strongly bound adsorbates on solid surfaces such as CO* and O* lose most of their gas-phase translational and rotational freedom upon adsorption. As a result, their thermal contributions to enthalpy and, in particular, entropy are significantly reduced compared to the gas phase. These systems are typically treated within the harmonic oscillator approximation, where the former translational and rotational motions are converted into vibrational modes, and chemical bonds are modeled as energetic springs described by a Hookean potential. Assuming that the pV term is small, which is often true for solids, we can write the enthalpy as:

$$H(T) = E_{\text{elec}} + E_{ZPE} + \sum_i \frac{\hbar \omega_i}{e^{\frac{\hbar \omega_i}{k_b T}} - 1}. \quad (2.61)$$

Furthermore, the entropy is given by:

$$S(T) = S_{\text{vib}} = k_B \sum_i \left[\frac{\hbar \omega_i}{k_B T (e^{\hbar \omega_i / k_B T} - 1)} - \ln \left(1 - e^{-\hbar \omega_i / k_B T} \right) \right] \quad (2.62)$$

While the ideal gas approximation is rather well-established for the thermodynamic description of gas-phase molecules, the harmonic approximation for adsorbates is often too

stringent and, depending on the system under study, anharmonic effects can significantly affect thermodynamic properties. In particular, the harmonic hypothesis of complete suppression of the translational degrees of freedom is not justified for weakly bound adsorbates, as 2D translation might still occur. The same goes for the rotational degrees of freedom, that might still be partially available provided that the rotation barriers are low. For such cases, the free/hindered translator and rotor models are more reliable thermodynamic frameworks, as they treat the $3N-3$ degrees of freedom of the system as vibrational modes while the remaining three are treated as two translational and one rotational.[159, 160] A further anharmonic effect of real systems is related to the shape of the actual interatomic potentials, that resembles more closely a Morse-type rather than a parabolic function. We expect the harmonic approximation, however, to yield accurate results for most of the adsorbates considered in this thesis such as CO^* , O^* , H^* and C^* , as they bind strongly to Co surfaces. A somewhat larger anharmonic contribution to the free energy might come from OH^* groups adsorbed on Co or Mn, as they typically retain more rotational motion upon adsorption,[161] but it is nevertheless not expected to significantly alter our results.

Part II.

Contents

3. Co Nanoparticles in Vacuum

As part of our effort to characterize the structure of Co FT catalysts, in this chapter we focus on the description of fcc-Co NPs in vacuum. This is important to first establish and validate our methodology, that will be expanded in Chapter 4 to also take into account the effect of the FT gas phase. Additionally, the results obtained here are more easily transferable to other catalytic systems, as they are not heavily dependent on the specifics of the FT process.

In the first section, we present our DFT - MC methodology to model metal NPs as a function of size and metal-support Interactions (MSI), which we put in action to simulate both free-standing and supported Co NPs upto 10 nm. In the second, we carry out a detailed characterization of the surfaces of the obtained models and systematically classify the plausible active sites, whose reactivities were probed by calculating direct CO dissociation pathways.

3.1. DFT-Monte Carlo Approach to Model Metal Nanoparticles

3.1.1. Introduction and Methods

Scope. In this section, we lay the foundations of our theoretical investigation as we present and validate the strategy employed throughout this thesis to produce structural models of Co metal NPs, which are the starting point of the results presented in section 3.2 and chapters 4 and 5.

The conventional way to model NPs is the Wulff construction, that has been previously to Co[63] but that was considered inadequate for the present application mainly because of its inability to capture size-effects, a crucial drawback when the focus is on structure-sensitive catalytic reactions such as Co FT. Conscious of this, previous theoretical studies elaborated other sophisticated computational techniques to address the task.[117–120] Van Helden et al. introduced a MC methodology to predict the equilibrium morphology of fcc Co NPs based on the coordination number (CN) of the constituent atoms.[117] Their analysis of particles in the 1–8 nm size range revealed that the fraction of step sites—commonly associated with CO activation—increases rapidly up to particle diameters of about 4 nm. Beyond this size, the proportion of B5-A sites was found to level off, whereas the fraction of B5-B sites continued to grow more gradually. On this basis, the authors proposed that the size dependence of the turnover frequency (TOF) of Co catalysts originates from the increasing density of active sites with particle size, although the predicted size at

which this correlation breaks down was smaller than that observed experimentally. Van Etten et al. subsequently developed a molecular dynamics (MD) framework to model the equilibrium shapes of Co NPs.[119] They parameterized a reactive force field (ReaxFF) using an extensive DFT dataset of Co configurations and employed simulated annealing to identify low-energy structures for particles ranging from 1 to 9 nm in size. To estimate size-dependent TOFs, they combined the calculated populations of surface sites with the corresponding CO dissociation barriers in a microkinetic model. Their results showed a pronounced increase in TOF with particle size up to roughly 5 nm, closely tracking the rise in the fraction of step sites, particularly of the fcc(110) type. In a subsequent study, a fictitious support was introduced into the MD simulations to assess the influence of metal–support interactions (MSI).[120] Varying the MSI strength was found to have little effect on the abundance of fcc(110) sites and, consequently, on the TOF, consistent with experimental observations that the size-dependent TOF behavior is largely insensitive to the nature of the support. Besides these works, numerous other studies have been devoted to the broader topic of metal NPs modelling for catalysis applications.[162–166] In this thesis, we elaborated a novel approach consisting of a computational workflow involving DFT and MC simulations. The former are used to derive an energy model whose sole descriptor is the first-shell CN of metal atoms, that is shown to perform remarkably well when benchmarked against DFT calculations. The energy model is then employed to estimate NPs energies in a MC algorithm that distributes metal atoms in a fixed crystal grid looking for low-energy structures, and we apply it to model Co NPs as a function of size and MSI. We further investigate the energetics of the simulated NPs and provide relevant surface energy (γ) and chemical potential (μ_{Co}) profiles.

The results presented in this section are adapted from the following publication:

Sireci, E.; Grüger, T. D.; Plessow, P. N.; Sharapa, D. I.; Studt, F. Modeling the Shape and Stability of Co Nanoparticles as a Function of Size and Support Interactions through DFT Calculations and Monte Carlo Simulations. *The Journal of Physical Chemistry C* **2025**, 129 (29), 13232–13243.

The author especially acknowledges the work carried out by MSc. **Tilman D. Grüger**, who wrote the MC code presented in this section and employed throughout the remainder of this thesis.

Methods. Spin-polarized DFT calculations were performed with the code VASP version 6.2,[167, 168] employing the GGA functional BEEF-vdW[135] and using the projector-augmented wave (PAW) method with standard PAW potentials.[169] Gaussian smearing with a width of 0.1 eV was used in all calculations and the sampling of the Brillouin zone was carried out in a Monkhorst-Pack grid with a k-points density of approximately 36 k-points per $\text{\AA}^{-3}$, that is a (14x14x1) grid for the (1x1) fcc-Co (111) surface. Bulk calculations were carried out with an energy cutoff of 600 eV, which was changed to 400 eV for all the other calculations. Convergence of the SCF cycle was set at an energy difference of 10^{-6} eV, while ionic convergence was achieved when atomic forces were below 0.01 eV/ $\text{\AA}$. The convergence threshold of the SCF cycle was reduced to 10^{-5} eV for the single point (SP) calculations carried out for the small NPs models. Surface energies were calculated by relaxing slab models from 8 to 10 layers thick and applying equation 3.1:

$$\gamma_{hkl} = \frac{E_{slab} - nE_{bulk}}{2A} \quad (3.1)$$

Where E_{slab} , n , A and E_{bulk} are the energy of the slab, the number of layers, the surface area and the energy of a bulk Co atom, respectively. The latter quantity was obtained through linear regression of E_{slab} vs. n , since this approach ensures high accuracy and fast convergence of the surface energy.[170] As shown in table , all the surface energies are well converged with slab thickness. Co(II) ions in CoTiO_3 , CoAl_2O_4 and Co_2SiO_4 considered in the DFT calculations of the adhesion energies (γ_{adh}) were treated with the Hubbard correction in the rotationally invariant approach introduced by Dudarev et al.[142] with $U_{eff} = 1.7$ eV, that was chosen to match the experimental oxidation enthalpies (ΔH_{rxn}) of Co to CoO as shown in Table A.1 and Figure A.1. Thermal corrections ($ZPE + \Delta\Delta H^{0 \rightarrow 500K} - T\Delta S$) were applied on the gas-phase reference molecules and the adsorbed hydroxyl groups on the support slabs within the ideal gas and harmonic approximations, respectively. Vibrational frequencies of the normal modes were calculated with the finite-differences method with atomic displacement of 0.02 Å.

3.1.2. Monte Carlo Algorithm

The core idea of the MC algorithm is to define a 3D grid of possible atomic positions corresponding to an ideal crystal lattice, and to distribute therein a user-defined number of atoms aiming at identifying low-energy configurations. The energy of the NP is equal to the sum of the energies of the atoms (E_{Co}) that compose it, that are estimated based on their CN. This is obtained by counting how many neighboring grid sites are occupied by other atoms. An extensive description of the employed energy model will be given in 3.1.3

The general workflow of the algorithm, graphically depicted in Figure 3.1, is the following:

1. The energy of the structure is evaluated;
2. An atomic move is randomly chosen;
3. The resulting energy change is evaluated;
4. The move is accepted or refused based on the Metropolis criterion (explained below) and the structure is updated accordingly;
5. Points 2 to 4 are repeated until the set number of iterations is carried out.

In each run, 5×10^{11} iterations are performed starting from a spherical arrangement of the atoms. Convergence tests (reported in Figure A.2) on the unsupported 10 nm particles, that is the largest size investigated, confirmed that this number of iterations yields well-converged NPs energies and site distributions. Based on the Metropolis acceptance criterion, a move is always accepted if it results in lowering of the energy, while if the final energy is higher it might be accepted based on a Boltzmann probability factor $p = e^{-\Delta E/(k_b T)}$.

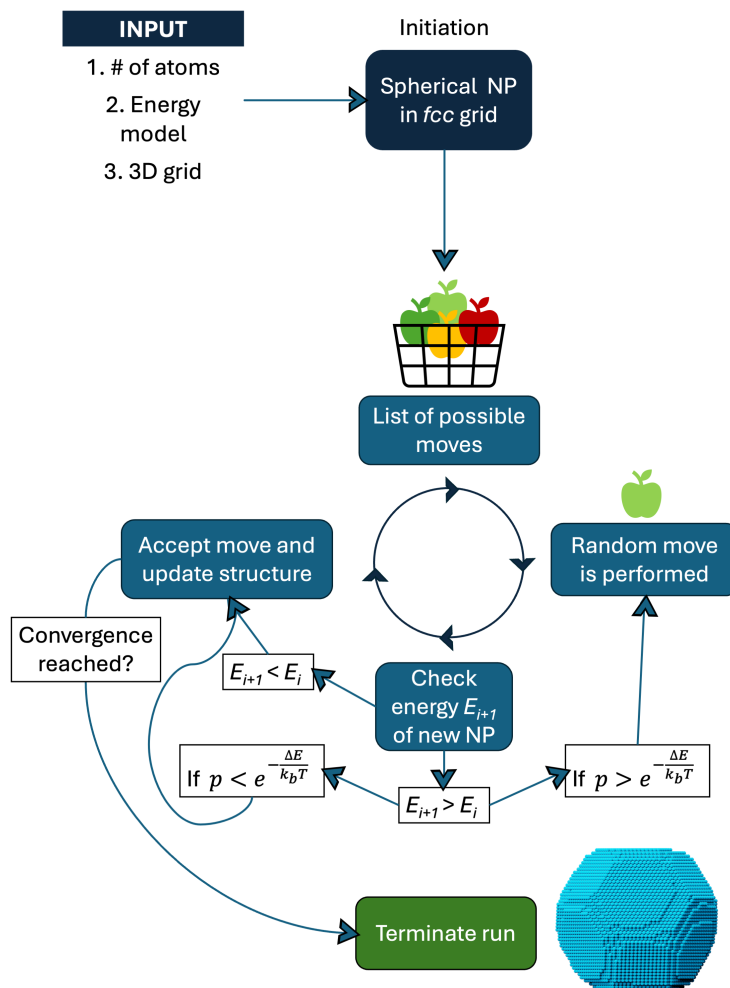


Figure 3.1.: Graphic depiction of the workflow of the MC algorithm. p is a random number between 0 and 1. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

The simulation temperature, that is entered as a used-defined input, hence determines the probability to accept energetically unfavorable moves. In all the runs, we applied a linear temperature decrease from $T = 5000$ K to $T = 500$ K over 90% of the iterations, while a constant temperature of 500 K was kept for the remaining 10%. The high starting temperature allows for fast rearrangement of the atoms from the initial configuration, which was found to speed up convergence. We simulated 2 (376 atoms), 4 (3008 atoms), 6 (10152 atoms), 8 (24064 atoms) and 10 nm (47000 atoms) NPs, and the respective number of atoms was chosen as roughly the number that would fit in a spherical particle of the corresponding size according to the equation below:

$$n_{atoms} = V^{sphere}(D_{Co})/V_m \quad (3.2)$$

where n_{atoms} is the number of atoms considered to reproduce an NP of diameter D_{Co} , $V^{sphere}(D_{Co})$ is the volume of a sphere with diameter D_{Co} , and V_m is the molar volume of Co. In this section, we followed the surface site identification scheme proposed by van Hardeveld and Hartog,[172] and thus we consider 2B3, B4, B5-A, B5-B, and B6 sites, that are listed in 3.2, and that largely correspond to threefold sites on fcc(111), fourfold sites on fcc(100), fivefold step sites in between (111) and (100) facets, fivefold step sites in between two (111) facets and sixfold kink sites, respectively. With this rather simple classification we are able to capture distinct atomic configurations that cover the whole NP surface. Nevertheless, in section 3.2 we will expand this scheme by considering further subcategories of low-coordinated, catalytically relevant fcc surface sites.

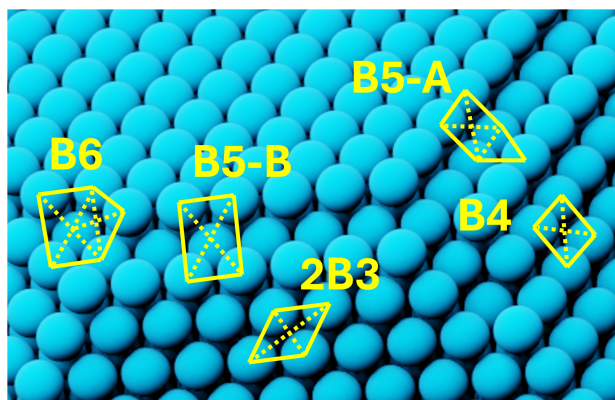


Figure 3.2.: Different atomic arrangements considered in this chapter are depicted on a Co NP. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

In order to obtain statistically meaningful results, 40 independent runs are carried out for each size. The reported site distributions and energies are the average from the 40 lowest-energy structures obtained in each run. The support was included in the simulations as a slab of dummy atoms oriented along the (111) surface in the fcc grid; stabilization arising from MSI is included by reducing the energy of Co atoms found in sites neighboring the support by γ_{adh} .

3.1.3. Energy Model Derivation and Validation

The energy of the NPs was evaluated as the sum of the individual energies of Co atoms (E_{Co}) that compose them. These were calculated based on the Co atom's first-shell CN under the assumption that E_{Co} scales linearly with CN, an approach that was put forward in a previous study [173] and that resembles a broken bond model.[174] We herein refer to this energy model as the CN model. The close-packed fcc (111) surface is composed of atoms with CN = 9; thus, by computing $\gamma_{(111)}$, we have obtained the energy difference between a Co atom in the bulk (CN = 12) and one with CN = 9, from which we derived the linear correlation depicted as the dashed blue line in Figure 5.8.

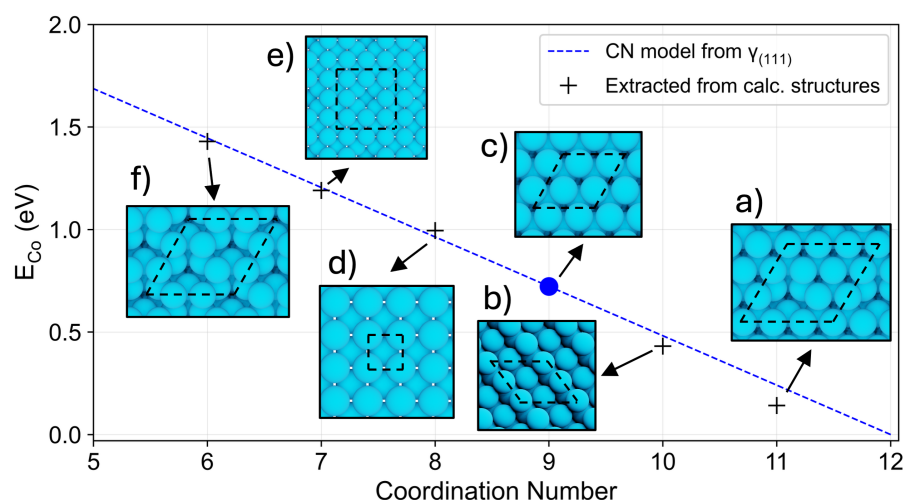


Figure 3.3.: E_{Co} with changing CN as predicted with the CN model and obtained from explicit calculations. The data points were obtained based on the following structures: (a) (111) surface with 1/9 monolayer (ML) vacancy density, (b) (311) surface, (c) (111) surface, (d) (100) surface, (e) (100) surface with 1/9 ML vacancy density, and (f) (111) surface with 1/3 ML vacancy density. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

We assigned an artificially high energy to atoms with $CN = 0$ to avoid their nonphysical detachment from the NP during the initial stages of the simulation. To assess the reliability of this framework, we compared our CN model with the explicitly calculated energies of Co atoms with different CN. These were estimated by calculating the surface energies of the mostly hypothetical structures depicted in Figure 5.8, from which we could retrieve the energies of Co atoms with $CN = 6, 7, 8, 10$, and 11 in addition to $CN = 9$ and 12 . The specifications relative to these structures are given in Table A.2. As shown in Figure 5.8, the CN model is in excellent agreement with the explicitly calculated E_{Co} , hence confirming that it is adequate to describe the energies of Co atoms in this CN range. However, extrapolating the CN energies to $CN = 0$ would yield a Co sublimation energy of 2.89 eV, significantly lower than the reported experimental value of 4.43 eV. This arises from the fact that, while the CN model assumes a fixed metal-metal bond energy regardless of CN, decreasing CN actually leads to an increase in bond strength.[175, 176] This was shown, among the others, by Methfessel and Scheffler[175] that, by employing a square-root fit, demonstrated that the linearity of the E_{Co} vs. CN relation breaks down for low values of CN. Nonetheless, in this work we are interested in the high CN range, since almost all the atoms in the NPs have $CN \geq 6$. We calculated with DFT the Co sublimation energy and obtained a value underestimated by only 3.5%, confirming that the discrepancy between experiments and the CN model is due to a breakdown of the model itself rather than inherent inaccuracy of DFT. Besides, it is worth noting that the BEEF-vdW functional was trained on a wide experimental dataset that contains metals (including Co) cohesive energies, which explains the high accuracy reported here.[135]

Since in our simulations we treat NP systems rather than periodic slabs, in Figure 3.4 we additionally report parity plots benchmarking the MC-predicted energies of ensembles of

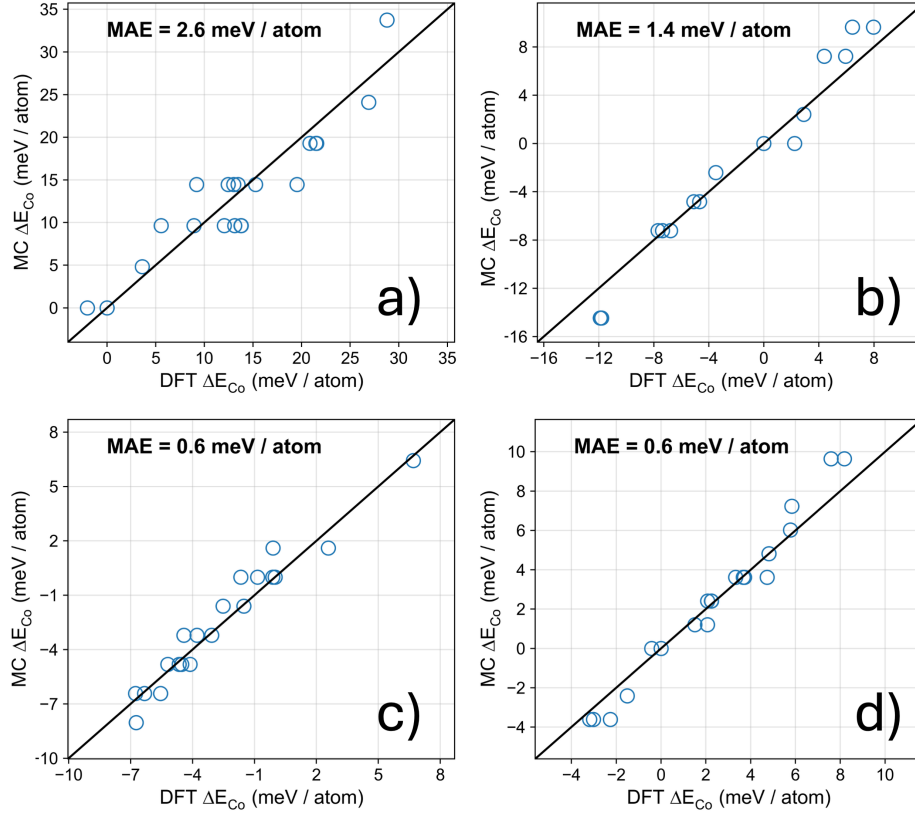


Figure 3.4.: Parity plots of MC vs. DFT-calculated ΔE_{Co} of (a) 100, (b) 200, (c) 300, and (d) 400 atom Co NPs obtained from short MC runs. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

15-20 particles containing 100, 200, 300, and 400 Co atoms against DFT energies calculated according to the following equation:

$$\Delta E_{Co}^{DFT} = E_{NPx}^{DFT} - xE_{bulk} \quad (3.3)$$

where ΔE_{Co}^{DFT} is the DFT-calculated energy of the NP with respect to bulk Co, E_{NPx}^{DFT} is the DFT-calculated potential energy of the NP, x is the number of atoms in the NP, and E_{bulk} is the DFT-calculated energy of one bulk fcc-Co atom. The MC and DFT ΔE_{Co} cannot be compared directly, since the former were computed from a model that considers a fully relaxed fcc(111) slab, while the latter were obtained from SP calculations on unrelaxed NP structures. Thus, for each NP size, we report the energy shift between the NPs and a reference NP structure that was chosen to minimize the MAE. It is worth noting that choosing any other structure would only cause a physically irrelevant shift of the data points in Figure 3.4. The structures used in the benchmark were obtained from short MC runs of 10^6 and 10^7 iterations for the 100 atoms and all the other NPs, respectively. This reduced number of iterations was necessary to ensure enough structural diversity because, for these small sizes, longer simulations cause the parallel runs to all converge

on approximately just two to three structurally different NPs. We show that the CN model performs increasingly well with increasing particle size, and already from NPs of 300 atoms, a mean average error of only 0.6 meV/atom is achieved, highlighting the very high accuracy achieved with this rather simple model.

3.1.4. Free-standing Co Nanoparticles

Snapshots of the converged Co NPs in the investigated size range are presented in Figure 3.5.

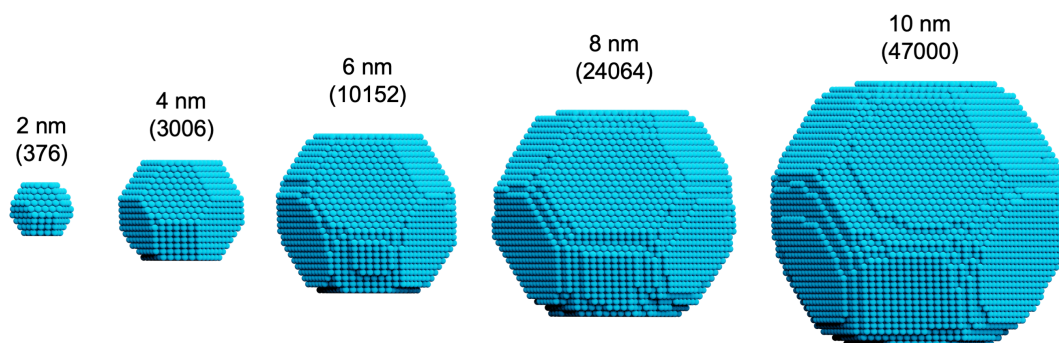


Figure 3.5.: Structural models of Co NPs obtained with the MC algorithm. The number of Co atoms composing the NPs are given in parentheses. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

All NPs assume a truncated octahedron (TO) shape, that predominantly expose (111) and (100) terraces. We observe that whereas on the small NPs the intersections between the terraces are mostly clean cut and give rise to well defined edges, on the larger ones irregular stepped domains become predominant. Accordingly, the site distribution analysis presented in 3.6 shows that the B5–A and B5–B step sites increase almost linearly in the investigated size range, as they are mostly absent on the 2 nm NPs and become 7.8 and 6.0% of the total sites, respectively, on the 10 nm particles. We additionally note that the B5–A sites are slightly preferred over the B5–B ones for $D_{Co} \geq 8$ nm. Furthermore, NPs size growth is accompanied by an increase in B6 kink sites, once again close to linear. These do not form any pseudo-ordered crystal facet, but are rather found on unterminated step/edge rows and can thus be thought of as surface defects. The emergence of defects depends on the tradeoff between the energy penalty and the gain in configurational entropy (S_{conf}) associated to their formation. Defects, in fact, are composed of low-coordinated atoms with $CN = 6$ and 7 and are thus unfavourable from a purely energetically standpoint. On the other hand, a defective surface has a much larger available configurational space than an ideal one. For example, a perfect Wulff crystal is characterized by $S_{conf} = k_b \ln(\Omega) = 0$, as there is only one possible atomic microstate corresponding to that system. The weight of S_{conf} on the overall NP stability increases significantly with particle size due to the steeply rising number of surface configurations, and ultimately leads to an increase of surface defects. The increase of S_{conf} with D_{Co} was qualitatively confirmed by carrying

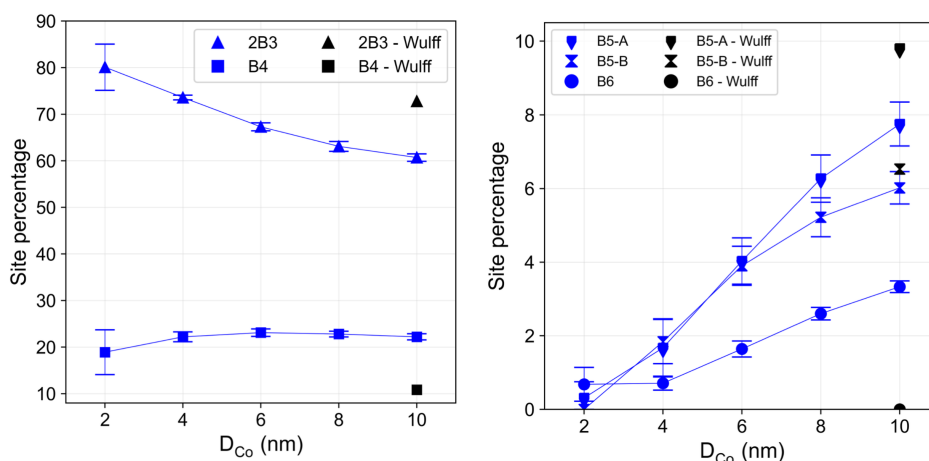


Figure 3.6.: Structural models of Co NPs obtained with the MC algorithm. The number of Co atoms composing the NPs are given in parentheses. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

out further MC simulations with increasing temperature while keeping track of the energy fluctuations and overall energy increase, that are correlated to the amount of different configurations explored by the system. These simulations consisted of 10^9 MC iterations at $T = 500, 1000, 1500,$ and 2000 K on the lowest-energy structures obtained for the different particle sizes.

As shown in Figure 3.7, with larger D_{Co} we witness larger energy increases and widths of the energy distributions, which reflect the increasing S_{conf} . As reported in Figure 3.6 the increase of B5-A, B5-B and B6 sites occurs at the expenses of 2B3 sites, that decrease from 80.1 to 60.7% in the investigated size range. On the contrary, B4 are mostly unaffected by D_{Co} and account for roughly 20% of the total. The experimentally reported structure sensitivity of FT Co catalysts can be rationalized based on the presented site distribution analysis. In particular, CO dissociation, often assumed to be rate-determining, has been shown by experiments and theoretical calculations to mostly occur on the step and especially kink sites, whilst the predicted barriers on (111) and (100) terraces are much larger and not matching kinetic studies.[63, 111, 115, 116, 177, 178] The increase of B5-A, B5-B, and B6 up until $D_{Co} = 10$ nm predicted here closely matches the experimental trends and reveal that the increase in TOF is due to larger surface concentration of the active sites as the particles grow in size. Our results are in qualitative agreement with the previous theoretical studies by van Helden and van Etten,[117, 119] albeit they predicted the site distribution to converge at $D_{Co} \sim 5$ nm, while the TOF is often reported to reach a plateau at $D_{Co} \sim 10$ nm. Despite being closer to experimental observations, our results indicate that the active sites concentration will likely increase for $D_{Co} > 10$ nm as the curves in Figure 3.6 do not appear to be significantly bending off with D_{Co} . This can be ascribed to the fact that, an increase in CO splitting sites does not always translate in an increase in TOF. This is because, as highlighted in recent microkinetic studies,[116] at a certain active site concentration the surface coverage of key intermediates might reach quasi

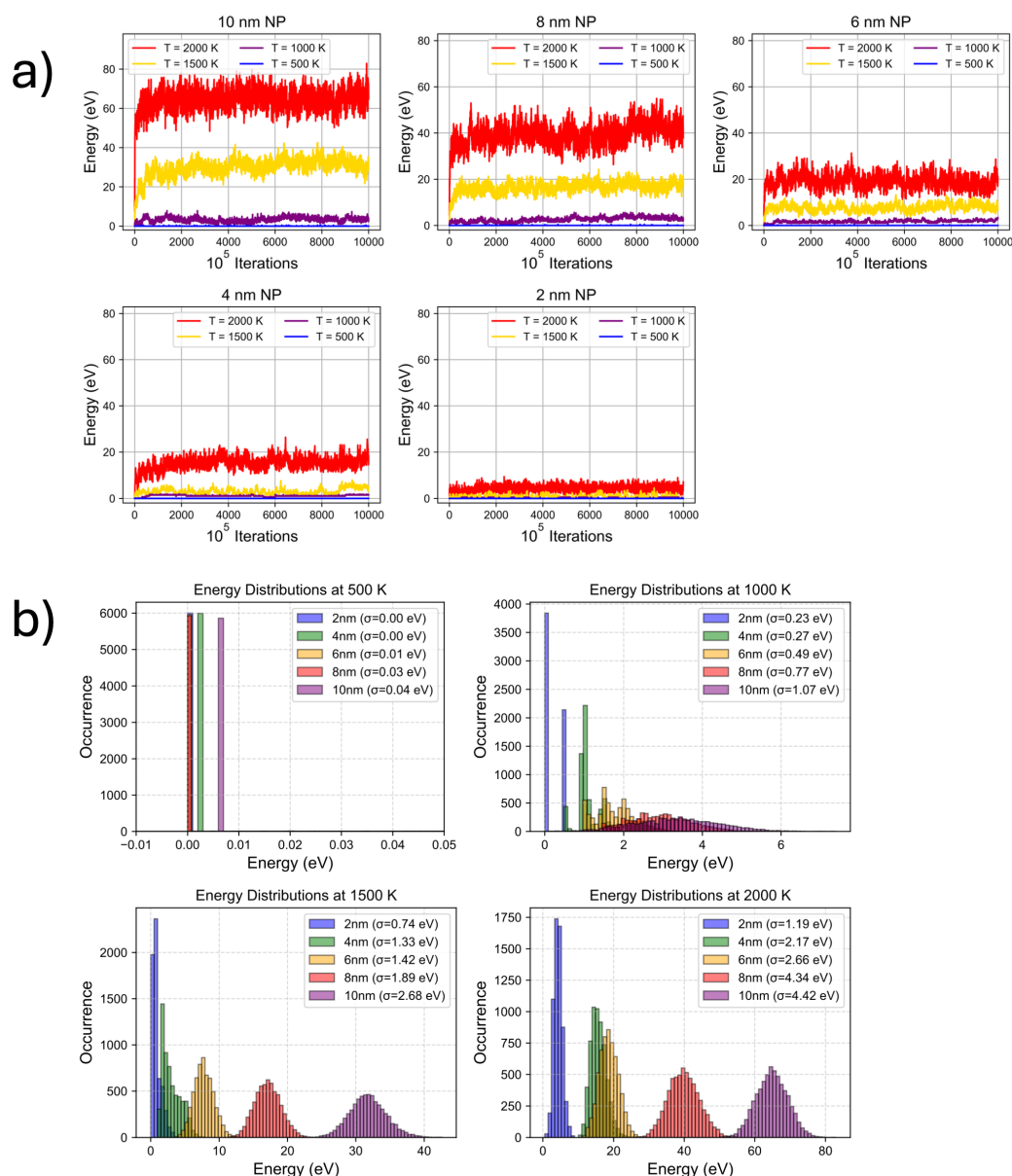


Figure 3.7.: NP energy (a) evolution and (b) distribution throughout 10^9 MC iterations carried out at $T = 500, 1000, 1500$ and 2000 K on the previously obtained global minima NP structures for the different sizes investigated. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

equilibrium, making further increases irrelevant in the reaction network. Besides this, in this chapter we only model Co NPs in vacuum, but will show in chapter 5 that CO causes drastic surface reconstruction that partially alters the trends reported here.

Furthermore, we were interested in how the outcomes of our simulations compare to the Co NPs obtained via the Wulff construction, that is the classical way to model crystalline NPs. In Figure 3.8a and 3.8b, we present the Wulff construction of fcc-Co NPs based on the calculated surface energies reported in Table A.2 and the corresponding atomistic model

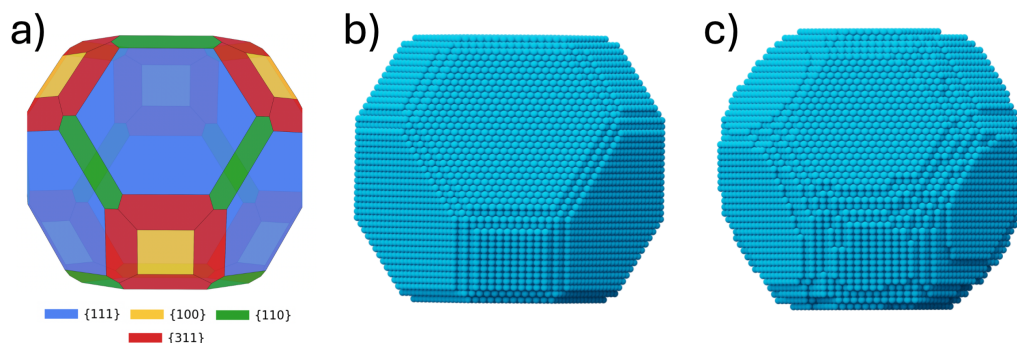


Figure 3.8.: (a) Schematic and (b) atomistic model of a 10 nm fcc-Co Wulff crystal computed based on the DFT-calculated surface energies found in Table S1 using the Python package Wulffpack[179] and (c) 10 nm Co NP produced via the MC algorithm. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

of a 10 nm NP, respectively. The resulting Wulff construction roughly resembles our MC particle, shown in Figure 3.8c, as they both assume a TO overall shape. In the former, large (111) terraces alternate with smaller (100) ones, and the stepped (110) and (311) facets are found at the (111)/(111) and (111)/(100) intersections, respectively. In Figure 3.6, we reported as black data points the site distribution of the resulting 10 nm NP atomistic model of the Wulff construction. We show that the Wulff particle has a higher concentration of 2B3 and B5-A sites, and a lower concentration of B4 sites with respect to the MC particle. Importantly, B6 sites are completely absent on the Wulff particle because the fcc(321) surface, where they are exposed, does not figure in the final construction and the approach is incapable of reproducing surface defects, that we point out to be the main source of B6 sites in the MC particle. This is an important drawback of the Wulff construction, especially in light of the very high CO-splitting activity of these sites. Below, we list further limitations of the Wulff construction approach that our methodology corrects:

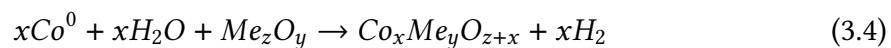
1. It cannot reproduce the effect of temperature on particle shape;
2. It can only report surfaces that are used as input by the user, introducing a significant bias;
3. It predicts only one equilibrium shape regardless of particle size, a crucial aspect when investigating structure-sensitive reactions such as FT.

These are key aspects in catalysis, that highlight important limitations of the Wulff construction and underscore that while it can be useful as a first-approximation description, it requires refinement when meaningful, in-depth explorations of catalytic systems are to be carried out. We believe our approach can offer this urgently needed upgrade, and could be routinely applied because of its computational cost-effectiveness, that comes from minimal requirements in terms of quantum-chemical calculations (only $\gamma_{(111)}$ needs to be computed) as well as by the very high speed of the MC simulations.

3.1.5. Supported Co NPs

3.1.5.1. Adhesion Energies Calculations

To improve the applicability of our models, we have also included the effect of the support in the MC simulations. To do that, it is necessary to calculate via DFT the adhesion energies (γ_{adh}) of Co on the chosen supports, that in our case are those most commonly employed in Co FT catalysts, namely α -SiO₂, γ -Al₂O₃ and TiO₂, both in the rutile and anatase phases. We have additionally considered the adhesion of Co on metal-support mixed oxides that might form at the interface, that are olivine Co₂SiO₄, spinel CoAl₂O₄ and ilmenite CoTiO₃. The Gibbs free energy of formation (ΔG^f) of the three compounds at 500 K, reported in table 3.1, were calculated as shown in eq.3.4-3.5:



$$\Delta G^f = E_{Co_xMe_yO_{z+x}} + x\mu_{H_2} - x\mu_{H_2O} - xE_{Co^0} - E_{Me_yO_z} \quad (3.5)$$

where $E_{Co_xMe_yO_{z+x}}$, E_{Co^0} and $E_{Me_yO_z}$ are the DFT-calculated potential energies of the bulk metal-support compound, bulk fcc-Co and bulk support, respectively, while μ_{H_2} and μ_{H_2O} are the chemical potentials of gas-phase hydrogen and water, respectively. These were calculated at typical FT conditions of T = 500 K, feed at 20 bar of composition H₂:CO = 2:1 and X_{CO} of 80%, leading to p_{H₂} = 2.0 bar and p_{H₂O} = 5.3 bar.

Table 3.1.: Gibbs free energy of formation ΔG^f for the Co-support mixed oxides at FT conditions (T = 500 K, p_{H₂} = 2.0 bar and p_{H₂O} = 5.3 bar).

Compound	ΔG^f (kJ/mol)
CoAl ₂ O ₄	-26
CoTiO ₃	-1
Co ₂ SiO ₄	42

γ_{adh} was calculated according to eq.3.6:

$$\gamma_{adh} = \frac{E_{int} - E_{slab}^{Co(111)} - E_{slab}^{support}}{A} \quad (3.6)$$

where E_{int} , $E_{slab}^{Co(111)}$, $E_{slab}^{support}$ and A are the DFT potential energies of the interface system, of the fcc-Co(111) slab, of the support slab and the interface area, respectively. In the interface models, we chose the following support facets:

- α -SiO₂(001), one of the low-energy facets in the crystal that was used in previous works;[180, 181]
- γ -Al₂O₃(110), the most abundant facet accounting for 70-80% of the total;[182, 183]
- Rutile TiO₂(110), the most abundant facet in the crystal;[184]

- Anatase $\text{TiO}_2(101)$, the most abundant facet that accounts for $\sim 90\%$ of the crystal surface;[184]
- Olivine $\text{Co}_2\text{SiO}_4(0001)$, that has the highest density of exposed Co atoms and thus more likely to be found at the interface;
- Spinel $\text{CoAl}_2\text{O}_4(110)$, that is isotropic to the $\gamma\text{-Al}_2\text{O}_3(110)$ surface, over which the mixed-oxide interlayer is expected to grow;
- Ilmenite $\text{CoTiO}_3(0001)$, experimentally reported to be the preferential crystal orientation in contact with hcp-Co(0001), analogous to fcc-Co(111).[185]

Different terminations were investigated for the $\text{CoTiO}_3(0001)$, $\text{Co}_2\text{SiO}_4(001)$, $\gamma\text{-Al}_2\text{O}_3(110)$ and $\text{CoAl}_2\text{O}_4(110)$, of which the most favorable have hydroxyl groups surface densities of 9.1 OH/nm^2 , 6.9 OH/nm^2 , 12.0 OH/nm^2 and 12.9 OH/nm^2 , respectively. These were hence used as reference states for the support slabs. The surface energies relative to the different terminations are found in Table A.3. When the investigated interfaces were either reduced or oxidized with respect to the reference states, μ_{H_2} and $\mu_{\text{H}_2\text{O}}$ were added in eq. 3.6 with coefficients depending on the interface stoichiometry. The specifications of the different interfaces and the resulting γ_{adh} are given in table 3.2. We observe that Co binds more strongly to the support in the order $\text{TiO}_2 > \text{SiO}_2 > \gamma\text{-Al}_2\text{O}_3$, which contradicts experimental observations that generally report increasing MSI in the order $\gamma\text{-Al}_2\text{O}_3 > \text{TiO}_2 > \text{SiO}_2$. [186–188] Nonetheless, Co-support compounds formation at the interface reconciles our results with experimental observations. Co binds more strongly to Co-containing supports, as confirmed experimentally by data collected for liquid Co droplets by Campbell et al. [189] and summarized by Rahmati et al., [190] according to which the γ_{adh} of Co on CoO is on average three times larger than on other common oxidic supports. We ascribe this to the formation of stable Co-Co metallic bonds between the support and the metal NPs. Co-support compound formation, that is more favorable in the order $\text{CoAl}_2\text{O}_4 > \text{CoTiO}_3 > \text{Co}_2\text{SiO}_4$, thus increases the Co adhesion and explains the experimentally reported trends of the MSI.

Table 3.2.: Supercells used in the calculation of adhesion energies, listed separately for metal and oxide surfaces. R90 and R60 indicate a rectangular and a parallelepiped unit cell, respectively. The strain coming from matching the two slabs sizes was always applied on the support.

Oxide		Metal		Strain on support (%)		Termination	γ_{adh} (meV/ $\text{\AA}^2$)
Surface	Supercell	Surface	Supercell	x	y		
$\alpha\text{-SiO}_2(001)$	$1 \times 2 \text{ R90}$	fcc (100)	$2 \times 7 \text{ R90}$	3.1	4.4	Dehydroxylated	−51
$\alpha\text{-SiO}_2(001)$	$1 \times 1 \text{ R60}$	fcc (111)	$2 \times 2 \text{ R60}$	3.2	3.2	Dehydroxylated	−41
$\alpha\text{-SiO}_2(110)$	$1 \times 1 \text{ R90}$	fcc (111)	$1 \times 2 \text{ R90}$	0.2	9.0	Dehydroxylated	−40
$\gamma\text{-Al}_2\text{O}_3(110)$	$3 \times 1 \text{ R90}$	fcc (111)	$2 \times 1 \text{ R90}$	3.6	3.7	Stoichiometric	+2
$\gamma\text{-Al}_2\text{O}_3(110)$	$3 \times 1 \text{ R90}$	fcc (111)	$2 \times 1 \text{ R90}$	3.6	3.7	+12 O	−39
Anatase (101)	$1 \times 7 \text{ R90}$	fcc (111)	$2 \times 12 \text{ R90}$	−3.4	−2.8	Stoichiometric	−37
Anatase (101)	$1 \times 7 \text{ R90}$	fcc (111)	$2 \times 12 \text{ R90}$	−3.4	−2.8	+14 O	−45
Rutile (110)	$3 \times 3 \text{ R90}$	fcc (111)	$2 \times 8 \text{ R90}$	0.9	−3.0	Stoichiometric	−47
Rutile (110)	$3 \times 3 \text{ R90}$	fcc (111)	$2 \times 8 \text{ R90}$	0.9	−3.0	+9 O	−64
$\text{CoAl}_2\text{O}_4(110)$	$1 \times 2 \text{ R90}$	fcc (111)	$2 \times 7 \text{ R90}$	5.5	0.6	Stoichiometric	−64
$\text{CoAl}_2\text{O}_4(110)$	$1 \times 2 \text{ R90}$	fcc (111)	$2 \times 7 \text{ R90}$	5.5	0.6	+6 O	−76
$\text{CoTiO}_3(0001)$	$1 \times 1 \text{ R60}$	fcc (111)	$2 \times 2 \text{ R60}$	−1.8	−1.8	Reduced	−103
$\text{Co}_2\text{SiO}_4(001)$	$1 \times 3 \text{ R90}$	fcc (111)	$1 \times 8 \text{ R90}$	−3.0	−4.6	Reduced	−66

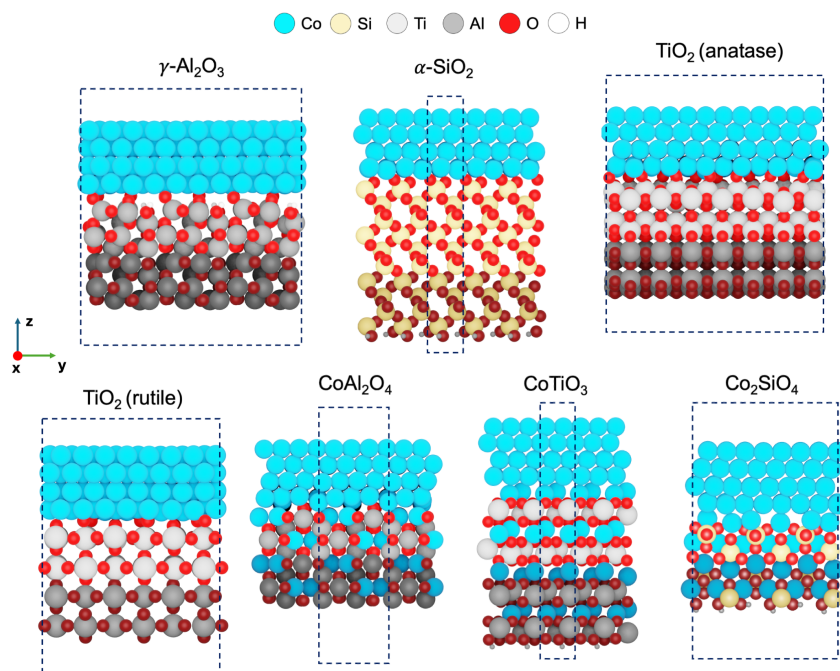


Figure 3.9.: Snapshots of the identified most favourable interfaces between Co(111) and the investigated supports. Shaded atoms were frozen during geometry optimization. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

In Figure 3.9 we show snapshots of the most favorable interfaces between Co(111) and the support slabs investigated. Throughout the reminder of this work, we will consider only three supports in the MC simulations, namely α -SiO₂(001), CoAl₂O₄ (110) and CoTiO₃ (0001). This is motivated by the calculated ΔG^f of the Co-support compounds as well as by previous experimental studies,[89, 191] but also because the three systems have significantly different γ_{adh} and thus serve as convenient case studies of weakly-, medium- and strongly-interacting supports.

3.1.5.2. Effect of the Support on Particles Shapes

Having calculated γ_{adh} , it is now possible elegantly include the effect of the support in our MC simulations that was included as a slab of dummy atoms oriented along the (111) planes. When a Co atom is found in a grid position adjacent to the support, its energy is reduced by γ_{adh} upon converting its units from meV/Å² to eV/atom according to eq.3.7:

$$\gamma_{adh} [\text{eV/atom}] = \frac{\gamma_{adh} [\text{meV}/\text{\AA}^2] \cdot n_{\text{Co}(111)}}{1000} \quad (3.7)$$

Where $n_{\text{Co}(111)}$ is the atomic surface area of the Co(111) surface equal to 5.4 Å²/atom. In Figure 3.10 we present the side view of 8 nm Co NPs on the three considered supports. Increasing γ_{adh} causes the NPs to increasingly flatten on the support to maximize the

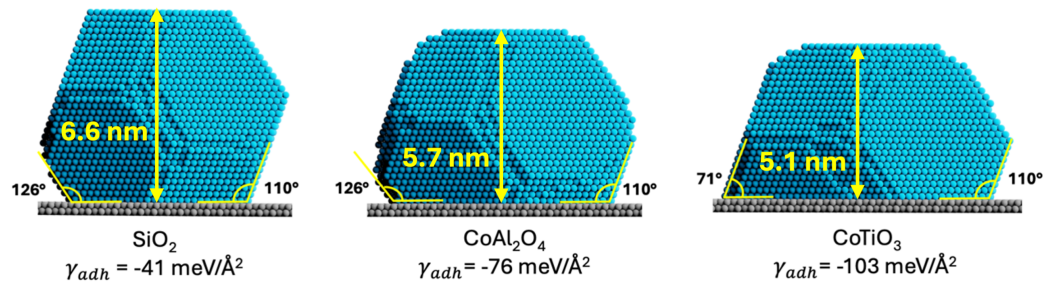


Figure 3.10.: 8 nm Co NPs on supports with increasing adhesion energy. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

Co-support interface, resulting in NP heights of 31 (6.3 nm), 28 (5.7 nm), and 25 (5.1 nm) atomic layers for the SiO_2 -, CoAl_2O_4 -, and CoTiO_3 -supported particles, respectively. As shown in Figure 3.11, γ_{adh} and the NP height to diameter ratio are approximately linearly correlated.

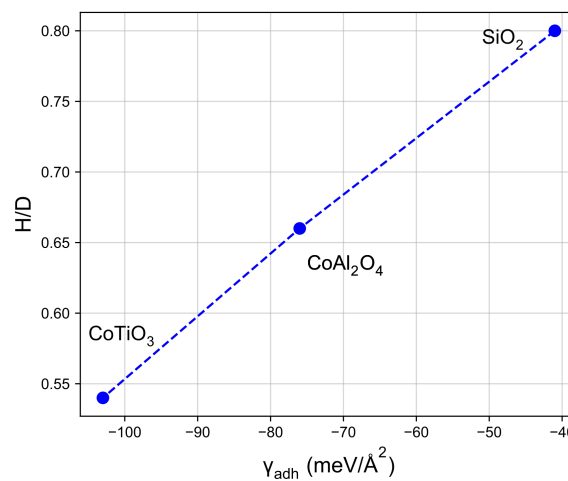


Figure 3.11.: The relation between γ_{adh} and the NP height to diameter ratio.

The NPs expose the lower (111) and (100) facets at the interfaces with the SiO_2 and CoAl_2O_4 supports with contact angles (θ) equal to 110 and 126°, respectively. On the CoTiO_3 support, however, the lower (100) facets completely disappear and only the lower and upper (111) facets figure at the interface, with $\theta = 110$ and 71°, respectively. As shown in 3.12, increasing MSI also slightly reduce the metal dispersion due to the growing number of Co atoms found at the support interface rather than on the NP surface, even though this effect becomes less prominent with growing D_{Co}

In Figure 3.13 we present the site distribution analysis of Co NPs with growing size. It is found that the MSI have hardly any effect on the NPs surface conformation, with the only

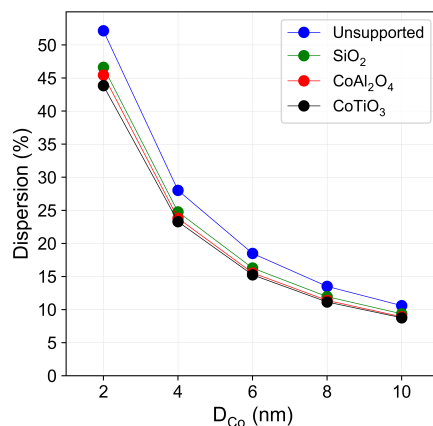


Figure 3.12.: Dispersion (defined as N_{surf}/N_{tot} , where N_{tot} and N_{surf} are the total number of atoms and number of surface atoms, respectively) of Co NPs increases with increasing D_{Co} and changing support. Error bars have been omitted as they are negligibly small. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

notable difference being that stronger MSI cause the particles to expose more 2B3 and less B4 sites, even though the percentages of the step and kink sites are largely unchanged.

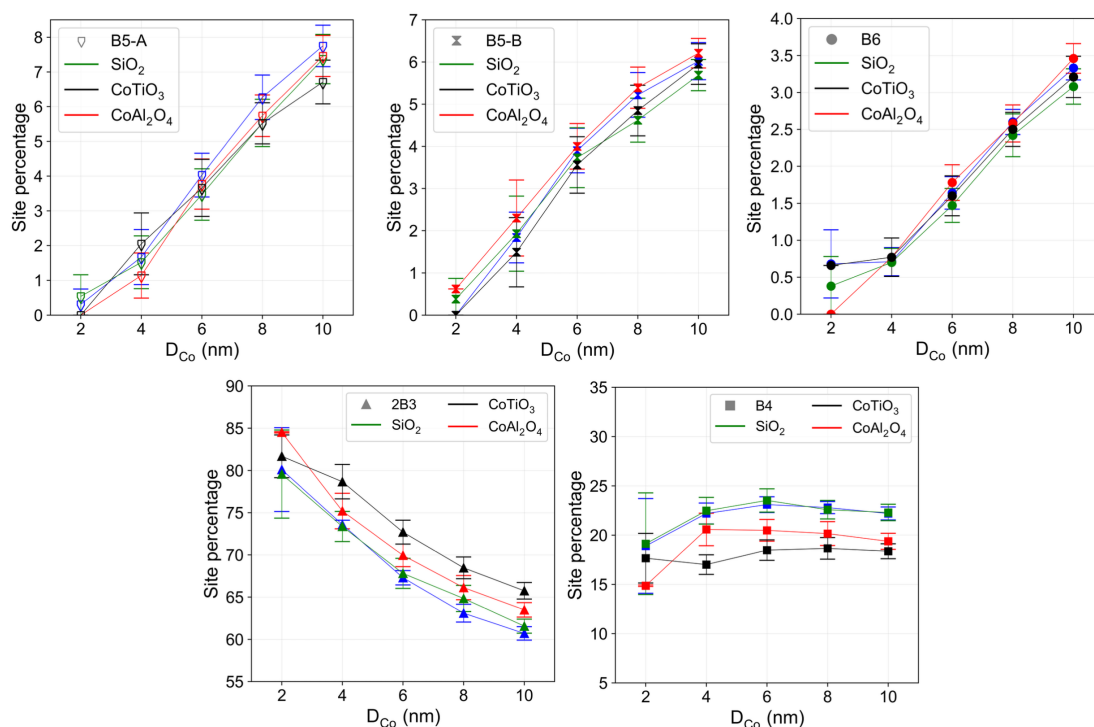


Figure 3.13.: Site distribution analysis for unsupported, SiO_2 -, $CoAl_2O_4$ - and $CoTiO_3$ -supported Co NPs with increasing diameter. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

Our results thus indicate that increasing γ_{adh} does not alter the intrinsic activity of the NPs, which is in agreement with the fact that the same structure sensitivity trends are reported

across studies employing different supports. Our results differ from those reported by van Etten[120] to the extent that they predict the NP shapes to be drastically influenced by changing MSI, even though they reach the same conclusions regarding TOF insensitivity on the MSI as the concentration of the fcc(110) site, that they predict to largely determine activity, is mostly unchanged. Lastly, we have tested how considering a different Co facet at the support interface would affect our results by simulating a fcc-Co(100)@ α -SiO₂(001) interface. Our results, presented in Figures A.3 and A.4, show that the NPs shapes are mostly unaffected by changing Co facet in contact with the support.

3.1.6. Energetics of Co NPs

While the overall shape of metal NPs has a large impact on catalyst activity, their stability highly influences catalyst resistance to deactivation. We hence complete our description of Co NPs in vacuum by investigating this aspect as a function of particle size and MSI and present the results in Figure 3.14.

In Figure 3.14a, we present the investigated Co NPs surface energies (γ) that were calculated as:

$$\gamma = \frac{E_{NP}}{A_{NP}} \quad (3.8)$$

Where the NP surface area A_{NP} was calculated as:

$$A_{NP} = \sum_i N_i A_i \quad (3.9)$$

With N_i , A_i and E_{NP} being the number of a generic site type, its surface area and the average energy over the 40 lowest-energy structures identified in each MC run, respectively. The calculated areas of the individual sites are 5.4, 6.2, 11.5, 8.8 and 11.8 Å² for the 2B3, B4, B5-A, B5-B and B6 sites, respectively. γ decreases with D_{Co} for all the particles due to decreasing concentration of low-coordinated atoms found at the edges and corners.[82, 189, 192, 193] We note that low-coordinated atoms are not only found on the B5 and B6 sites, that increase with D_{Co} , but also on edges and corners, that arise from clean cuts between the terraces and do not fall in the site categories investigated earlier. As it will be shown in Chapter 5, the concentration of these sites is high on the small NPs and drastically increases their γ , in agreement with several previous studies. We further observe that the different curves of γ converge with particle size from relatively small $D_{Co} = 6-8$ nm, because the increase of B5 and B6 sites concentration with size mitigates the decrease of corners and edges, preventing γ from diminishing further. The relation obtained by Rahmati et al.[190] for perfect cuboctahedral NPs converges on similar γ values as the ones predicted here, but it does so more slowly because the increase of steps and kinks with D_{Co} is not taken into account. We note that the MSI have a rather small effect on γ , in agreement with the similar site distributions of the NPs across the different

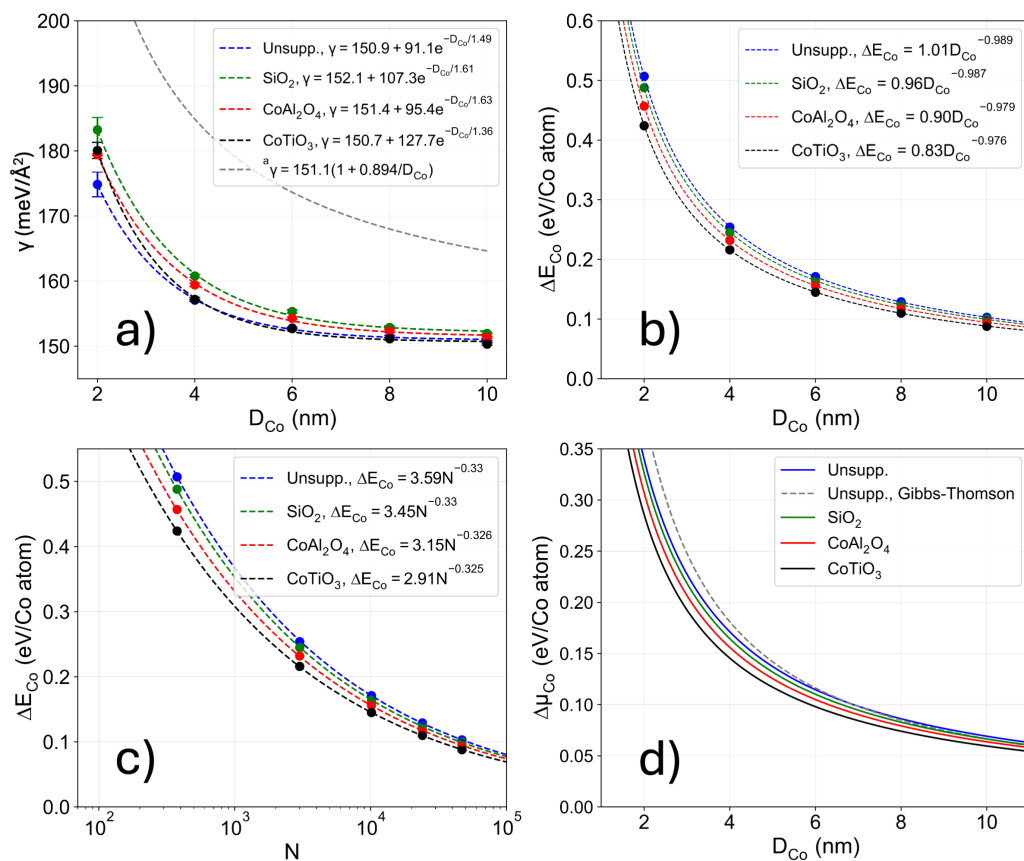


Figure 3.14.: a) Surface energies of Co NPs with increasing D_{Co} on different supports. b) Average energy per atom ΔE_{Co} with respect to bulk Co with increasing D_{Co} and c) with increasing number of atoms (N). d) Chemical potential of the Co NPs $\Delta\mu_{Co}$ with increasing D_{Co} . The Gibbs-Thomson derived $\Delta\mu_{Co}$ was calculated via Equation 7 using the size-dependent surface energy of the free-standing particles. a) Relation proposed by Rahmati et al.[190] to predict the γ of Co NPs. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

supports. Nevertheless, the supported particles are characterized by slightly higher γ as compared to the unsupported ones due to the fact that they expose a larger number of low-coordinated atoms at the Co-support interface. Among the supported NPs, stronger adhesion to the support slightly decreases γ because of the higher concentration of 2B3 at the expenses of B4 sites shown in Figure 3.13. Furthermore, we observe that all the curves of γ converge on a value of ~ 151 meV/Å², which is very close to the experimental value of 157 meV/Å² (2.51 J/m²) reported by Tyson.[194] This close agreement corroborates the soundness of our methodology, but is somewhat surprising in light of the widely reported underestimation of γ by GGA-DFT functionals.[195] Nonetheless, we note that this notion is often reinforced by comparing experimental surface energies with those calculated for the fcc(111) and hcp(0001) metal slabs, which are the most stable facets for both crystals. Besides the large uncertainty associated with the experimental measurements of γ , to the best of our knowledge these studies do not measure the energy of any specific crystal facet, but rather of a hypothetical average low-index surface.[194] This highlights that, when comparing experimental γ to those calculated for the close-packed fcc(111), an

underestimation is to be expected and does not necessarily stem from inaccuracies of DFT, even though across different functionals relatively large ranges of γ are typically obtained. In Figure 3.14b we additionally report the Co NPs energies per atom (ΔE_{Co}) with increasing D_{Co} . These can be accurately fit by hyperbolic-like functions, reflecting the ΔE_{Co} dependency on the surface:volume ratio. As expected, increasing MSI stabilize the NPs, even though this effect is more pronounced for the smaller particles due to the proportionally higher amount of Co atoms found at the interface. We then used the curves of ΔE_{Co} against total number of atoms (N) shown in Figure 3.14c to derive the relations between the Co NPs chemical potential ($\Delta\mu_{Co}$) and D_{Co} , reported in Figure 3.14d, as per equation 3.10:[193]

$$\Delta\mu_{Co} = \left(\frac{\delta(N \times \Delta E_{Co}(N))}{\delta N} \right)_{T,p} \quad (3.10)$$

Similarly to ΔE_{Co} , we observe that increasing γ_{adh} lower $\Delta\mu_{Co}$, indicating a stabilization of the particles. Interestingly, as this effect is once again more pronounced the smaller the NPs, the curves in Figure 3.14d become less steep as the interactions with the support become stronger, which correspond to a reduction of the thermodynamic driving force for sintering.[196] Stronger MSI thus hinder sintering both from the thermodynamic and kinetic standpoints, as they also increase the diffusion barriers for NPs as well as metal adatoms.[181, 197] Finally, in Figure 3.14d, we compare the $\Delta\mu_{Co}$ obtained from our models from that obtained via the Gibbs-Thomson relation:[198, 199]

$$\Delta\mu_{Co} = \frac{2\gamma V_m}{R} \quad (3.11)$$

Where we used the γ relation for unsupported NPs displayed in Figure 3.14a. Besides a slight overestimation in the low D_{Co} range, this analytical relation yields very similar results to those obtained from our simulations. We note, however, that often the bottleneck of using the Gibbs-Thomson relation is to obtain accurate estimates of γ , as most studies either neglect its dependency on particle size[200–202] or rely on theoretical models based on ideal NP structures.[82, 192] On the other hand, we believe our approach advances the description of the stability of metal NPs because it yields rather precise relations for γ and $\Delta\mu_{Co}$ taking into account the effects of particle size, temperature, the presence of surface defects and the influence of the support.

3.1.7. Conclusions

In this section, we have presented our methodology to model metal NPs applied to the case of fcc-Co with special focus on the Fischer-Tropsch synthesis. The most remarkable feature of this approach is the extensiveness of the resulting description of NPs shapes and stability against a very small computational cost. This was enabled by the simplicity of the underlying energy model, that for the unsupported NPs only requires one descriptor, i.e. the CN of Co atoms, which can be obtained with extremely cheap quantum chemical

calculations. For the supported particles, just one additional parameter (γ_{adh}) must be provided. Despite its simplicity, the model demonstrated excellent performance when benchmarked against DFT calculations. The scientific soundness of the methodology was confirmed by the agreement between the predicted evolution of the surface site distribution with particle size and the experimentally reported structure-sensitivity of the TOF of Co catalysts in the Fischer-Tropsch synthesis. In particular, the increase of step and kink sites matches almost quantitatively the reported increase of the TOF, and the predicted insensitivity of the surface conformation with changing MSI mirrors the fact that the same experimental trends are reported across different supports. Besides matching previously reported data, the description presented here also gives new insights that can be extrapolated to other catalytic systems such as the link between higher surface defects concentrations on large particles with their higher S_{conf} and the early convergence of γ with particle size. Additionally, we have provided precise relations for γ and $\Delta\mu_{\text{Co}}$ that were previously lacking. The fact that our approach relies on a fixed crystal grid implies that it is not suitable to reproduce amorphous domains. Additionally, due to the fact that the support local environment is blurred in the dummy atoms representation, we would not be able to predict the effect of specific support motifs on the final NP structures. We believe nevertheless that these effects become relevant for $D_{\text{Co}} < 1$ nm, which is below the size range investigated here.

As mentioned in the scope of this section, the work presented here is the starting point of many of the results presented throughout this thesis. In Section 3.2 we will systematically classify the surface sites present in our models and probe their reactivity, in Chapter 4 we will expand the methodology to account also for the effect of the CO gas phase, and in Chapter 5 we will predict the structure and stability of the Mn promoter on the NP models produced here.

3.2. Systematic Investigation of Active Sites in FCC Metal Nanoparticles

3.2.1. Introduction and Methods

Scope. A number of fundamental chemical processes such as ammonia synthesis,[203–205] methanol synthesis[206–208] and the FT reaction [30, 32, 209] heavily rely on catalysts consisting of supported TM NPs. While the underlying mechanism of some reactions such as ammonia synthesis are now well understood,[210–212] those of other processes such as FT are still vividly debated.[19, 111, 177, 213]

Due to its excellent accuracy-computational cost tradeoff, DFT has become the workhorse in computational chemistry to study and shed light on reaction mechanisms in catalysis.[214–216] Nonetheless, one of the main limitations of DFT calculations in heterogeneous catalysis is the choice of the active site model.

The simulations carried out in 3.1 revealed that metal NPs are characterized by a diverse landscape of surface sites arising from the different crystal facets, their intersections as well as defects and irregularities. Despite this, in computational models of chemical reactions it is customary to rely on just a handful of low-index stepped surfaces such as the fcc(211) and fcc(110), that are considered as prototypical active sites regardless of particle size. In this section, we aimed at going beyond this approximation by systematically classifying the plausible active sites of fcc metal NPs. We then probed their reactivities by calculating direct CO dissociation pathways and identify sites that are significantly more active than the ones reported in the literature to date, underscoring the enhancement in predictive power when full, realistic models of NPs are available. Additionally, we show that the particle size largely influences the nature of the active sites, and that conventionally employed step sites mostly fail to represent the active site landscape of small particles, that are actually largely populated by edges and corners.

The results presented in this section are adapted from the following publication:

Sireci, E.; Sharapa, D. I.; Studt, F. A Comprehensive Overview of Active Sites of Fcc-Co Nanoparticles and Their Role in CO Splitting—A DFT Study. *The Journal of Physical Chemistry C* **2025**, 129 (49), 21634–21641.

Methods. All the DFT calculations were performed with the same settings as described in 3.1. Additionally, the TS search was carried out using the improved dimer method as implemented in VASP,[217] for which we used the same energy and force convergence thresholds as for the other geometry optimizations. In all calculations, we considered four layers slab models, where the bottom two layers were frozen in the bulk fcc-Co configuration. All the calculations are carried out in the low coverage regime, being 1/5 for the fcc-Co(641) surface, 1/4 for the fcc-Co(321) and corner surfaces and 1/3 for all the others when only step atoms are considered. We note that the definition of coverage is rather arbitrary for some surfaces such as the ones where corners are modeled. We made sure, however, that the coverage of CO when normalized to all surface atoms is small (always below 1/12 CO molecule per surface Co atom) and that adsorbed CO molecules are always separated by at least 7.5 Å, except for the edge B2 where the CO images are 7.1 Å apart. All models had at least 15 Å of vacuum in the z-direction. All the reaction pathways are corrected for zero-point energy (ZPE) contributions. Vibrational analysis to estimate ZPEs were carried out with the finite differences method with atomic displacements of 0.02 Å, and only include the adsorbed CO. All TSs were confirmed through a vibrational analysis that yielded only one imaginary frequency located along the reaction path.

3.2.2. Classification of Low Coordinated Sites

While in the previous section we employed a rather broad classification of surface sites, here we identify several more distinct surface motifs that are highlighted in Figure 3.15 on a 4 nm (left) and 8 nm (right) free-standing Co NPs. We note that we only focus on the low-coordinates sites (LCS), since the 2B3 and B4 terrace sites often display high

reaction barriers with respect to the LCS and are already extensively used in computational models.

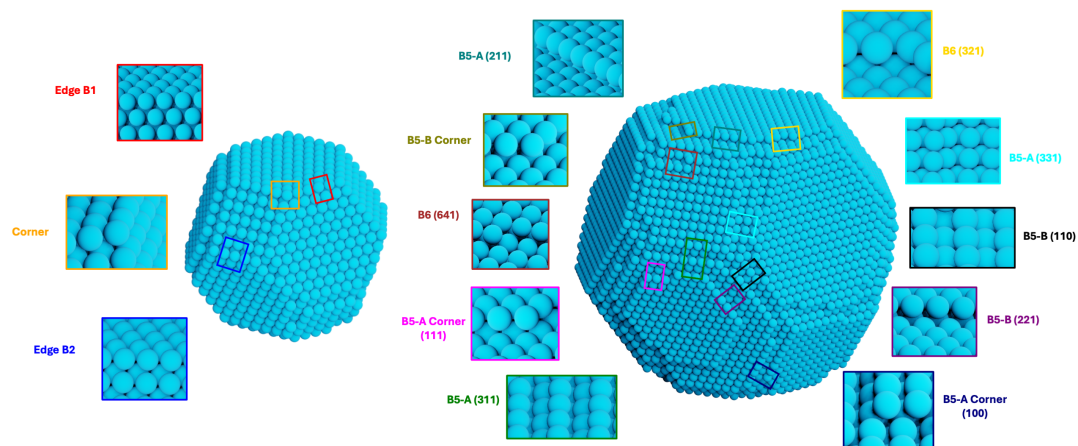


Figure 3.15.: The considered sites highlighted on a 4 (left) and 8 (right) nm NPs. Reprinted from Ref. [218] with permission. Copyright 2025 American Chemical Society.

As shown in Figure 3.15, the 4 nm NP mostly exposes corner sites and the two types of edge sites, i.e. the Edge B1 and Edge B2, located at the (111)/(111) and (111)/(100) intersections, respectively. On the other hand, on the 8 nm NP many more surface motifs were identified. We considered several subcategories of the previously employed B5-A, B5-B and B6 sites, and in particular we highlight five different B5-A, three B5-B and two B6 sites. B5-A step sites are located at the intersections between (111) and (100) terraces. In the updated scheme, when they are found in two or more consecutive step rows, they are classified as B5-A (311). Alternatively, they can exist on a (111) or a (100) terrace and are classified as B5-A (211) sites and B5-A (331) sites, respectively. B5-A sites adjacent to corners were additionally denoted as B5-A Corner (111) or B5-A Corner (100) depending on whether they are located on a (111) or (100) terrace. B5-B step sites are found at the intersections between two (111) terraces. Similarly to B5-A sites, when they are found in two or more consecutive step rows they are classified as B5-B (110), while when they are found on a terrace, they are called B5-B (221). B5-B sites next to a corner are classified as B5-B corner sites. Lastly, the two identified types of B6 kink sites are the B6 (321) and B6 (641), located on (111) and (100) terraces, respectively.

As already evident in Figure 3.15, the occurrence of the different sites changes drastically with particle size. This is quantified in Figure 3.16a, where the relative percentages of each site as a function of D_{Co} are presented. In particular, while the LCS for $D_{Co} < 6$ nm are predominantly edges and corners, these are increasingly exchanged with steps and kinks as the particles grow bigger. The two types of edge sites are by far the most common LCS in the low D_{Co} size range and, even if they decrease steeply for $D_{Co} > 4$ nm, they still account for roughly 10% of the total LCS on the 10 nm NP. Except for the 2 nm particles, the Edge B2 sites are more abundant than their B1 counterpart. This is because,

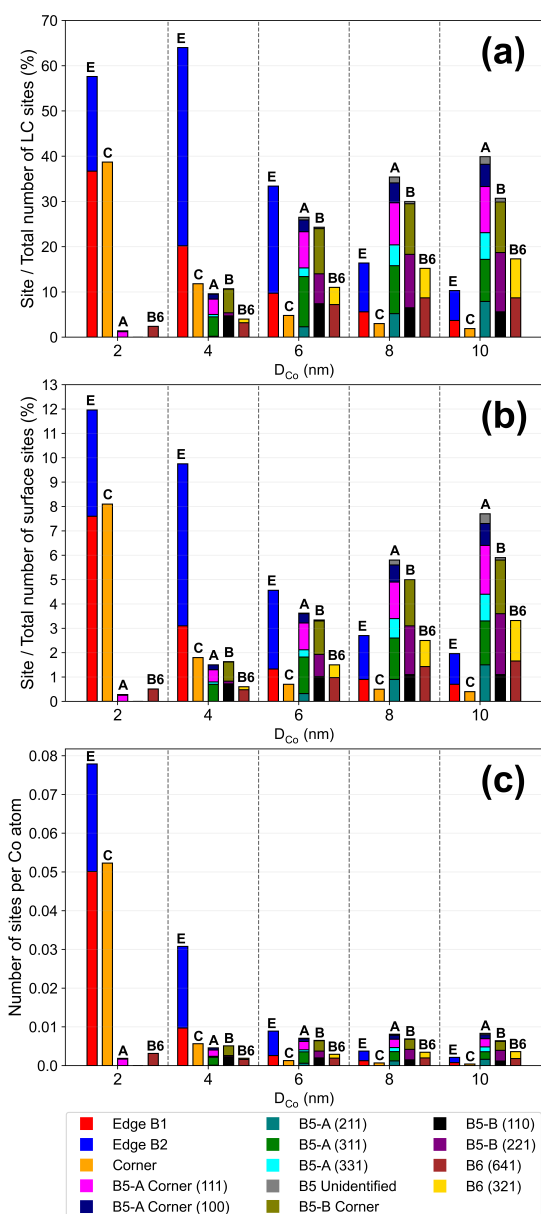


Figure 3.16.: Percentages of each of the considered sites with respect to (a) the total number of low-coordinated sites and (b) the total number of surface sites. (c) number of sites per number of Co atoms in the NP with increasing particle diameter (D_{Co}). Reprinted from Ref. [218] with permission. Copyright 2025 American Chemical Society.

in the overall TO NP shape, there are 24 (111)/(100) intersections, where the Edge B2 sites are located, against only 12 (111)/(111), where the Edge B1 sites are found. Corner sites are also very common on the 2 nm NPs, but their concentration drops as the particles grow bigger and already from $D_{Co} = 6$ nm they account for less than 5% of the total. With growing D_{Co} , B5-A and B5-B step sites, that are always present in similar proportions even though the former grows somewhat faster, become predominant. These sites are the most diverse, and, while in the smaller particles rows of steps (B5-A (311) and B5-B

(110)) are more common, individual step rows (B5-A (211) and B5-B (221)) corrugating the terraces increasingly appear as the particles grow bigger. B6 are mostly absent in the smallest particles, where their presence is ascribed to the fact that the fixed, non-magic number of atoms (376) used in the simulations makes it impossible to accommodate all atoms without creating a few irregularities. In real catalysts, however, it is likely that the small particles can self-assemble into clusters with a well-defined number of atoms that is regulated by detachment of the ones that are in excess. As already shown in section 3.1, B6 sites increase steadily with D_{Co} and peak at $\sim 17\%$ of the total LCS for the 10 nm NP. The B6 (321) are mostly absent on the small particles, but grow faster than the B6 (641) type resulting in the two sites being present in similar proportions for $D_{Co} = 10$ nm. This analysis provides guidance in choosing relevant surface models based on the particle size distribution of the catalytic system under scrutiny. In particular, it is worth noting that the conventionally employed periodic surfaces (fcc(211), fcc(110) etc.) likely fail to describe reality when the particles are smaller than 5 nm, where these sites are in practice mostly absent. In Figure 3.16b we show the percentage of the different LCS normalized to the total number of surface sites, which also include the 2B3 and B4 terrace sites. The initial decrease of edge and corners is later counterbalanced by the increase of B5 and B6 sites, which causes a minimum in the surface concentration of LCS for $D_{Co} = 6$ nm. This explains also the reported trend for the number of LCS normalized to the number of Co atoms shown in Figure 3.16c, characterized by an initial fast decrease of the cumulative number of LCS with particle size that stays roughly constant for $D_{Co} > 6$ nm. We can correlate this to the trend of the Co NPs γ shown in Figure 3.14a: without the increase of step and kink sites, that is not taken into account in the relation derived for perfect cuboctahedral NPs, γ would still decrease significantly for $D_{Co} > 6$ nm following the decrease of edge and corner sites. However, this decrease is actually canceled out by the simultaneous increase of steps and kinks, that determines the early convergence of γ .

3.2.3. Probing the Reactivity for CO Activation

LCS are usually the most active sites in metal NPs. Bond unsaturation tends to shift upwards the d-band center, strengthening adsorption of reactants as well as key intermediates.[219] Additionally, LCS offer particularly favorable reaction pathways because of their open geometries, which reduce lateral interactions and repulsion between reacting molecular fragments of a TS.[52] Nevertheless, LCS are not all equivalent and can display different activities depending on the reaction. Reactions where sigma bonds are to be cleaved or formed, often in hydrogenolysis steps, occur on just one or two metal atoms and are similarly catalyzed by edges and corners as by steps and kinks. On the other hand, reactions where strong double or triple π bonds are activated—as in the dissociation of diatomic molecules such as CO, N₂ and NO—the stabilization of the TS requires more complex geometries where several metal atoms are involved, and are significantly more favorable on step and kink sites. Importantly, this causes different reactions to display different types of structure sensitivity. The TOF in methane activation, that belongs to the first category, decreases with increasing particle size,[220–222] in agreement with the

decrease of the cumulative LCS in the $D_{Co} < 6$ nm range shown in Figure 3.16b, whilst FT follows the opposite trend, as CO dissociation, that occurs on steps and kinks, is likely rate-determining.

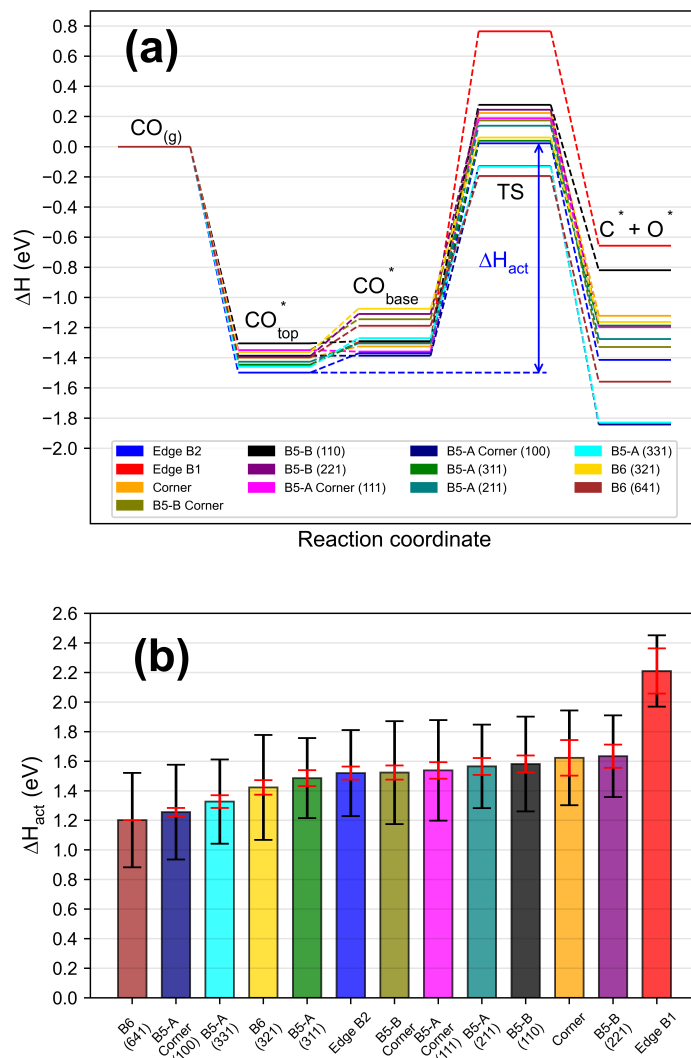


Figure 3.17.: (a) Reaction enthalpy diagram ($T = 0$ K, ZPE included) for direct CO dissociation on the different types of LCS and (b) bar plot of the activation enthalpies ($\Delta H_{TS} - \Delta H_{top}$). The relative enthalpies in b) are calculated based on the ΔH_{act} for the B6 (641) site, error bars for both the absolute and relative activation enthalpies are the standard deviations obtained from the energies calculated with the 2000 GGA functionals of the BEEF-vdW ensemble. Reprinted from Ref. [218] with permission. Copyright 2025 American Chemical Society.

Having classified the different LCS on fcc metal NPs, we probed their reactivities by calculating direct CO dissociation pathways, shown in Figure 3.17, where CO first adsorbs on a top position, then migrates to the base of the considered site and finally splits in C^* and O^* . As shown in Table A.4, except on B6 (641) and B5 corner (111) sites, the most favorable CO adsorption site was always on top, in agreement with surface science experiments at low-coverages both on Co terraces and steps.[223–226]

We present the calculated TSs in Figure 3.18, which can be classified based on the binding mode of C to the Co atoms in three categories. In the first, that only applies to the edge B1 site, C binds to a threefold site; in the second, which occurs on all B5-B sites, C binds to a non-planar fourfold site; and in the third, that is relative to all the B5-A, B6, edge B2 and corner sites, C inserts in a square planar Co site. Furthermore, the reactivities of the different sites are compared among each other in the bar plot of Figure 3.17b, where the error bars –that are the standard deviations obtained from the ensemble of 2000 hypothetical GGA functionals built-in in the BEEF-vdW method– inform us on the uncertainty of the calculations, both in terms of absolute and relative values of ΔH_{act} . It is found that the calculated ΔH_{act} span across a wide ~ 1 eV energy window, even though just one site (the Edge B1) is particularly unreactive and all the others fall within a ~ 0.4 eV range. Strikingly, the binding mode of C seems to largely influence the reactivity, as the only site where it is located on a threefold site is by far the least reactive, those where it binds to the non-planar fourfold sites are mostly found on the low-reactive side of the plot and the most active sites are those where C binds to the planar square site. This underscores the high stability of this configuration, whose effect dominates the reactivity of Co catalysts but also their surface reconstruction, as we will show in Chapter 5. The possibility of tetra-planar coordinated (TPC) carbon structures was first postulated by Hoffmann et al.[227] more than 50 years ago and, since then, several molecules containing this functionality have been synthesized, with the Al_4C^{2-} anion being a well-understood case. [228–230] The same model was more recently applied to explain the extraordinary stability of TPC C embedded in metal surfaces.[231] The high stability of the square-planar M_4C (where M is a generic metal) configuration is due to a special case of double aromaticity that is established in this chemical environment, where the $2p_z$ atomic orbitals (AOs) of C overlap with the metal π radial states, satisfying the Hückel’s rule for aromaticity ($4n + 2$) with $n = 0$, while the $2s$, $2p_x$ and $2p_z$ AOs overlap with the σ radial metal states satisfying the Hückel’s rule with $n = 1$. The metal acts as an electron reservoir and thus gives or takes electrons to enable the double aromaticity, which determines a baseline energetic gain that is similar across all metals. On the other hand, the system-specific electron count determines the occupancy of the antibonding states, that become more populated the higher the electron count. It has been shown that Co has an optimal electron count that explains the high stability of the Co_4C configuration with respect to other metals such as Ni, Cu, Rh, Pd and Ag, and motivates both the proneness to reconstruction/carbidization of Co surfaces upon C deposition and the high reactivity of LCS with square planar sites reported here.

Interestingly, among the three sites (Edge B1, B2, and corner sites) that are predominant on the small particles, the Edge B2 is the only one that displays a reasonable $\Delta H_{act} = 1.52$ eV, which is close to that of many Co step sites, long thought to be active for CO dissociation. Thus, the low barrier of the Edge B2 site is at odds with the observed structure sensitivity of Co catalysts, as it implies that even the smallest particles should showcase relatively high FT activity. In this regard, we postulate that high CO coverage under FT conditions might significantly hinder the reaction on the Edge B2 sites with respect to step sites. These, in fact, present pockets which are likely not covered under operating conditions and that are absent on the Edge B2 sites. Thus, although the Edge B2 sites are in principle as

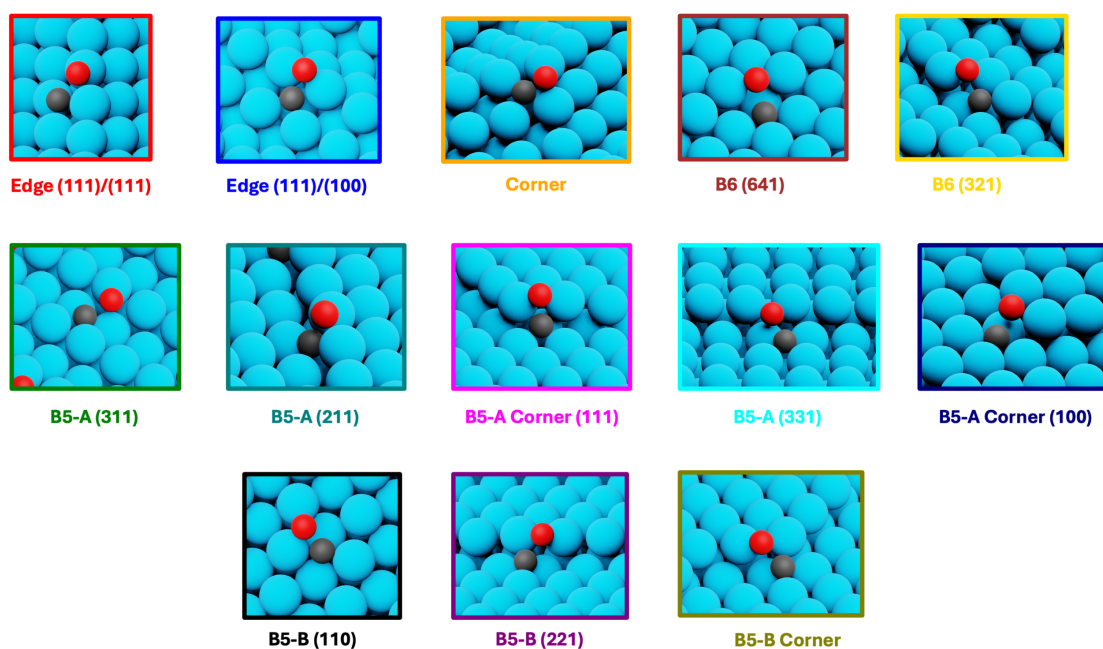


Figure 3.18.: Snapshots of the calculated TSs on the 13 LCS identified in this work. Reprinted from Ref. [218] with permission. Copyright 2025 American Chemical Society.

active as the step sites, they might not offer adjacent free Co atoms that are necessary for CO to dissociate. On the other hand, we have also identified four LCS –the two B6 and the B5-A corner (100) and B5-A (331) sites– that are significantly more active than the Edge B2 and that are increasingly concentrated as the particles grow bigger, and could thus be those responsible for the observed structure sensitivity. To the best of our knowledge, the most active LCS considered in this work, i.e. the B6 (641), was never considered before to model direct CO dissociation on fcc-Co catalysts and is at least 0.2 eV more active than the most active fcc site reported in the literature to date, namely the B6 (321).[111] Under FT conditions, such difference in barrier results in $\sim \times 100$ speedup in reaction rate, that would significantly alter the outcomes of microkinetic models. In this context, we believe that having at one’s disposal realistic structural models of metal NPs makes it more likely that catalytically relevant sites are properly taken into account in theoretical calculations.

The objective of our study was to carry out a fast, qualitative screening of the reactivity of the identified LCS, using direct CO dissociation on fcc-Co NPs as case study. Nonetheless, we acknowledge that neglecting effects such as surface reconstruction, realistic CO coverage and the presence of the hcp phase limits the transferability of the results reported here to technical catalysts. Hence, we stress that this analysis was not intended to provide a detailed mechanistic understanding of the FT reaction.

The black error bars in Figure 3.17b reveal that there is a large uncertainty in terms of the calculated absolute values of ΔH_{act} , as the standard deviations obtained via the BEEF-vdW ensemble calculations range between 0.24 and 0.36 eV, showing that accurate quantitative predictions are largely unattainable at the GGA level of theory for direct CO dissociation. Nonetheless, the uncertainty is greatly reduced when the activity of the different LCS are

compared among each other. This is shown by the standard deviations of the various ΔH_{act} relative to the B6 (641) site, reported as red error bars in Figure 3.17b, that are drastically smaller and mostly fall within a 0.05 eV energy range, highlighting the accuracy of DFT when comparing trends.[232, 233]

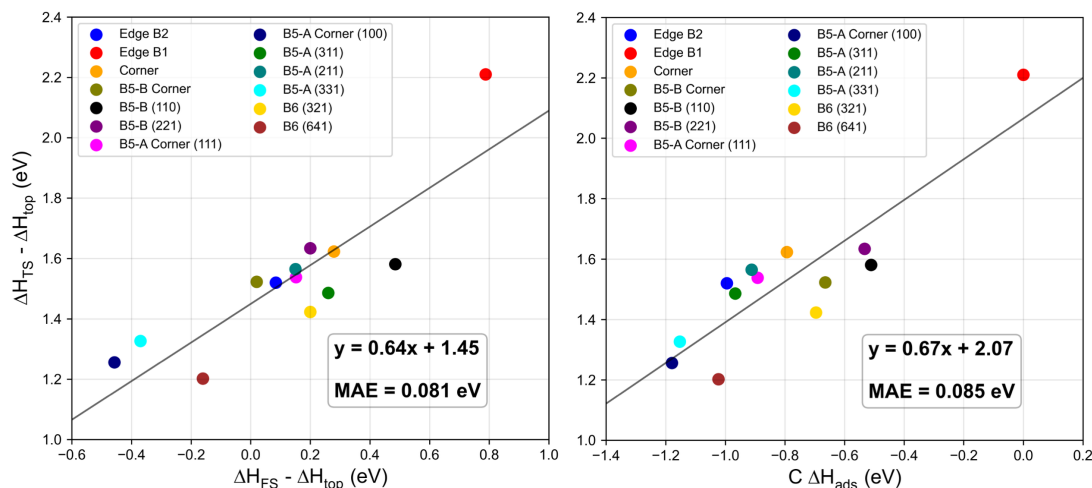


Figure 3.19.: Brønsted-Evans-Polanyi (BEP) relation for direct CO dissociation on the low-coordinated sites investigated in this study (left) and correlation between ΔH_{act} and C adsorption (right). “MAE” stands for mean absolute error, where the error of each individual data point is the length of the normal segment connecting the point and the correlation line

In the left panel of Figure 3.19, we show that the reactivity of the different sites is well described by the Brønsted-Evans-Polanyi (BEP) relation,[234–236] with the exception of the least active edge B2 site where the TS lies significantly above the correlation line. Another, albeit smaller, outlier is the most active B6 (641) site, where the TS lies below the correlation line. The most stable FSs are those for the B5-A (331) and B5-A corner (100) sites, likely because both C and O occupy fourfold sites, which are the most favorable ones for both species. Furthermore, as shown in the right panel of Figure 3.19, the reactivity of LCS correlates well with C adsorption, underscoring the previously discussed importance of the C adsorption mode in determining direct CO dissociation rates.

3.2.4. Conclusions

In this section, we have performed a detailed classification of the surface sites appearing in our NP models and identified a constellation of different LCS in fcc metal catalysts of different particle sizes. Additionally, we probed their reactivities by calculating direct CO dissociation barriers and have shown that not all LCS are equivalent, as reaction barriers may differ by up to 1 eV. The importance of setting up theoretical calculations based on realistic models of NPs was readily demonstrated by the identification of three sites that, despite showcasing higher activity than the most active site reported in the literature to date, were never considered to model direct CO dissociation pathways. Furthermore, we have shown that the fcc(211) and fcc(110) surfaces conventionally employed to model the

active sites of metal NPs fail to represent reality when NPs below 6 nm are considered, as their surfaces are predominantly populated by edges and corners. More generally, this section provides guidance in choosing realistic active sites models based on the particle size distribution of the catalyst under scrutiny, that was largely lacking and we anticipate could resonate in the computational catalysis community.

4. Co Nanoparticles in the Fischer-Tropsch Gas Phase

In Chapter 3 we have established our methodology to model metal NPs and have shown how this enhances the predictive power of the simulations. While the previous conclusions are rather transversal to most catalytic systems based on supported metal NPs, in this chapter we dive deeper into the realm of Fischer-Tropsch by considering the effect of its gas phase on Co NPs structures and stabilities.

In the first section, we show how our CN-based energy model was modified to take into account the effect of CO, and characterize the resulting Co NPs similarly to what was done in Section 3.1.3. In the second, we calculate the diffusion paths of Co subcarbonyl species on the γ -Al₂O₃ and TiO₂ supports and derive the relative diffusion barriers. These were then implemented along $\Delta\mu_{\text{Co}}$ profiles in simulations that predict the particle size distribution evolution due to sintering via Ostwald ripening over industrially relevant time scales of FT operation. Our results indicate that strongly adsorbing molecules can crucially affect structure-activity relationships and deactivation mechanisms, and should hence be included in computational models, that can be elegantly done within our DFT-MC framework.

4.1. Effect of CO on Co NPs Shapes and Stability

4.1.1. Introduction and Methods

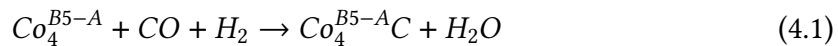
Scope. Both our results presented in Chapter 3 and those of the works by van Helden et al.[117] and by van Etten et al.[119, 120] have only treated Co NPs vacuum. Nonetheless, previous experimental and theoretical studies have indicated that the Co NPs surfaces might reconstruct during FT,[42, 237, 238] due to the strong adsorption of CO and the high pressure. In this section, we aimed at going beyond the limitations of the previously discussed works by expanding our approach to also account for the effects of Co-CO interactions. This was done by calculating CN-specific energy corrections based on the adsorption free energies (ΔG_{ads}) of CO on different Co facets, that were then used to modify our energy model. Our simulations reveal that Co NPs undergo drastic surface rearrangement upon Co adsorption, which also considerably alters their surface energies and chemical potential profiles.

Our methodology can now consider simultaneously the effects of particle size, MSI and of the gas phase, yielding a remarkably comprehensive description of Co NPs under operating conditions at a moderate computational cost.

The results presented in this section are adapted from the following publication:

Sireci, E.; Grüger, T. D.; Plessow, P. N.; Sharapa, D. I.; Studt, F. Modeling the Shape and Stability of Supported Co Nanoparticles under Fischer-Tropsch Conditions via DFT Calculations and Monte Carlo Simulations: Insights into CO-Driven Surface Reconstruction. *Catalysis Science & Technology* **2025**, 15 (22), 6703–6715.

Methods. The DFT calculations were carried out with the settings described in Chapter 3. In the ΔG_{ads} calculations, we considered four layer Co slabs, of which the bottom two were frozen in the bulk configuration. The slabs were separated by their periodic images in the z direction by at least 15 Å of vacuum. In order to account for thermal corrections, the reference gas-phase molecules were treated with the ideal gas approximation, while the harmonic approximation was used for the adsorbed CO molecules on the Co slabs. Vibrational analysis were carried out as described in Chapter 3. The (111) and (100) terraces were considered to calculate the corrections for Co atoms with CN = 9 and 8, while the stepped (311) surface was used to represent atoms with CN = 7. As mentioned in Section 3.2.3, TPC C in Co fourfold sites is an exceptionally stable configuration, and was predicted by Banerjee et al.[238, 239] to induce nanoislands formation on the (111) terraces. Thus, hereby we consider C insertion in the fourfold site at the base of B5-A sites by introducing an energy correction for Co atoms with CN = 10, that are found almost exclusively in these atomic arrangement. Since C does not adsorb in adjacent sites, this correction was obtained by halving the ΔG_{rxn} calculated according to Equation 4.2:



$$\Delta G_{rxn} = \Delta G_{Co_4C} + \mu_{H_2} - \mu_{H_2O} - \Delta G_{CO@(311)} \quad (4.2)$$

We considered the CO-covered (311) surface to model the B5-A sites. It is worth noting that this correction is the only one that also depends on p_{H_2O}/p_{H_2} . To model Co atoms with CN = 5 and 6, we formed triangular and hexagonal corners on the (311) facet where we adsorbed one CO molecule on top position. Finally, we applied a fixed correction of -0.6 eV to Co atoms with CN = 1, 2, 3 and 4. We note that these atoms might appear during the initial stages of the simulations but are absent in the low-energy structures. We did not apply any correction for the Co atoms with CN = 11 and 12 as they were assumed to be inaccessible to CO. We mimicked industrial FT conditions by considering T = 500 K and a feed of 20 bar of composition $H_2:CO = 2:1$ at X_{CO} of 25% and 75%, representative of a low and high X_{CO} regimes, respectively. The first corresponds to $p_{CO} = 5$ bar and $p_{H_2O}/p_{H_2} = 0.2$, while the second to $p_{CO} = 1.5$ bar and $p_{H_2O}/p_{H_2} = 2.1$. In the presence of CO, we can think of the metal-support interface formation as a process in which we first need to clean the Co surface from the adsorbed CO. To account for this, the values of γ_{adh} calculated in Section 3.1.5.1 were reduced by the ΔG_{ads} of CO on the fcc(111) surface normalized per Co atom ($\Delta G_{ads}^{(111)}$).

4.1.2. CO Adsorption on Co Surfaces

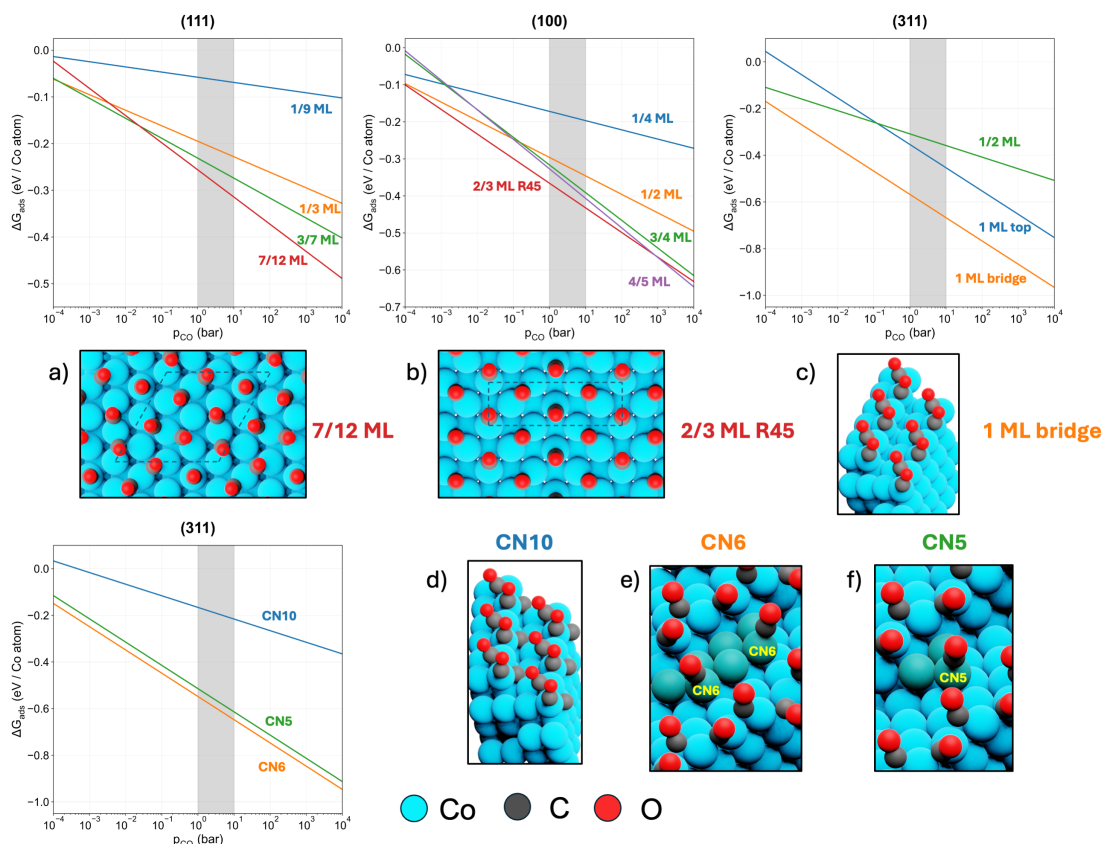


Figure 4.1.: Phase diagrams at 500 K of CO coverages on different Co surfaces and most stable arrangements under relevant FT conditions of a) (111), b) (100) and c) (311) fcc Co facets. Configurations used to calculate ΔG_{ads} for Co atoms with CN = 10, 6 and 5 are shown in d), e) and f), respectively. Turquoise Co atoms in e) and f) constitute the hexagonal and triangular corners. Shaded areas in the plot roughly indicate the p_{CO} range under industrial FT conditions. Reproduced from [240] with permission from the Royal Society of Chemistry.

In Figure 4.1, we present the calculated phase diagrams of CO adsorption at 500 K on the different Co facets and snapshots of the most stable surface arrangements under typical FT conditions. We qualitatively reproduced the results by Gunasooriya et al.[241] for the (111) facet, as we predict the same transitions from 1/3 ML to 3/7 ML and from 3/7 ML to 7/12 ML, albeit shifted to lower p_{CO} values. Additionally the calculated most favorable coverage of 7/12 ML under FT conditions is close to that of 0.5 ML extrapolated from experimental measurements reported by Weststrate et al.[242]. In this arrangement, one CO occupies a top position and the remaining six occupy bridge positions in the unit cell. Since accurate estimations of CO adsorption energies are notoriously challenging for GGA functionals,[195, 243] we also calculated the low-coverage (1/9 ML, with CO in a top position) heat of adsorption (including ZPE contributions) of CO on Co (111) and obtained a value of -135 kJ/mol (-1.41 eV), which is close to the experimental value of -128 kJ/mol reported by Papp[224] for the analogous hcp (0001) surface and underscores, as previously noted,[244] the excellent results obtained via the BEEF-vdW functional in terms of CO

adsorption energy calculations. On the (100) surface, we report an equilibrium coverage of 2/3 ML, where CO molecules are equally split between top and bridge positions. A significantly higher coverage of 1 ML is found on the (311) surface, where the bridge binding mode is preferred over the one on top because it reduces lateral interactions. We note that the same arrangement was reported for the stepped hcp-Co (10-10) facet.[226]. For the Co atoms with CN = 5, 6 and 10 only one surface configuration was considered. The calculated energy corrections were included into the energy scheme elaborated in Section 3.1.3, that was thus modified as shown in Figure 4.2 and was employed in our MC algorithm to produce the structural models of Co NPs under FT conditions. As expected, in the CN range 7-10 the ΔG_{ads} of CO decreases with decreasing CN, in agreement with experiments.[223–225, 245]. Interestingly, ΔG_{ads} is shown not to decrease further for CN = 6 and 5. The correction for CN = 10 due to C insertion is the smallest among the one considered and also the most sensitive to X_{CO} , as it increases by ~60% upon switching from the high to low conversion scenarios.

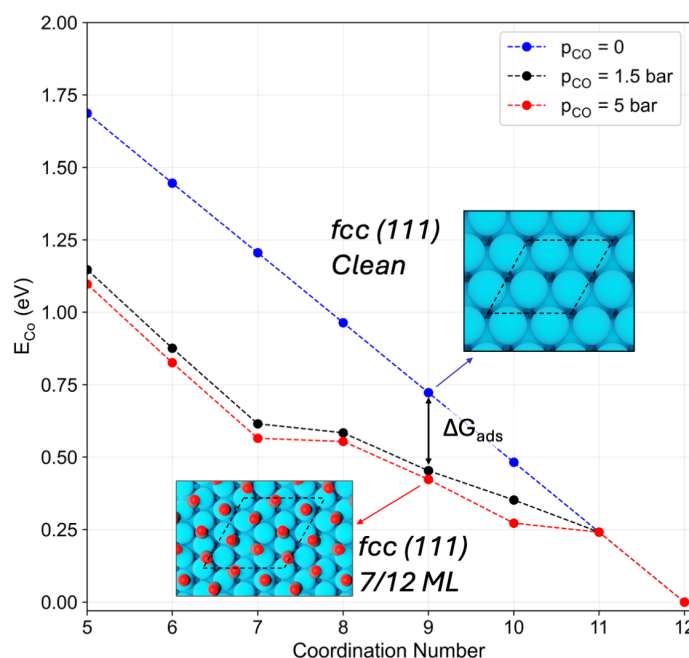


Figure 4.2.: E_{CO} scaling with CN with increasing p_{CO} . Reproduced from [240] with permission from the Royal Society of Chemistry.

The underlying assumption made in our calculations that H_2 and the FT reaction intermediates can be neglected is justified by considering that CO is by far the strongest-binding adsorbate and, therefore, it is the predominant species populating the Co surface. This is confirmed by recent microkinetic models[116] that revealed that, under FT conditions, the fcc(111) Co terraces are covered for ~54% by CO, and only for ~5% by all other species. According to the same study, the B5-A sites are only covered for ~46% by C, that together with CO is the only adsorbate considered in this chapter.

In Table 4.1.2 we additionally report the CO stretching frequencies for the 15 structures considered in this study. For each CO position, we obtain a range of frequencies depending

Table 4.1.: CO stretching frequencies on different Co facets at the different coverages considered in this study. These were calculated considering each CO molecule in the unit cell individually, i.e. by freezing all the atoms except one CO molecule. We employed a scaling factor of 1.008 for all the computed frequencies, that was chosen ad hoc to match the experimental CO stretching frequency in the gas phase of 2143 cm^{-1} . For the inserted C in the fourfold sites of the (311) facet, all three identified normal modes are reported.

	Top (cm^{-1})	Bridge (cm^{-1})	Hollow (cm^{-1})	Inserted C (cm^{-1})
(111) – 1/9 ML	1973	–	–	–
(111) – 1/3 ML	1970, 1970, 1970	–	–	–
(111) – 3/7 ML	2002	–	1768, 1788	–
(111) – 7/12 ML	2015	1852, 1853, 1853, 1855, 1855, 1856	–	–
(100) – 1/4 ML	1985	–	–	–
(100) – 1/2 ML	1984, 1985	–	–	–
(100) – 2/3 ML R45	1991	–	–	–
(100) – 3/4 ML	2003, 2003, 2007, 2007	1879, 1880	–	–
(100) – 4/5 ML	2009, 2012, 2023, 2024	1886, 1887, 1899, 1904	–	–
(311) – 1/2 ML CO	2003	–	–	–
(311) – 1 ML CO Top	1987, 2013	–	–	–
(311) – 1 ML CO Bridge	–	1895, 1920	–	–
(311) – 1 ML CO Bridge + 0.5 ML C	–	1904, 1928	–	703–612–386
CN6	1989, 1994	–	–	–
CN5	2016	–	–	–

on Co surface and coverage that are $1970\text{--}2023\text{ cm}^{-1}$, $1870\text{--}1920\text{ cm}^{-1}$ and $1768\text{--}1788\text{ cm}^{-1}$ for top, bridge and hollow positions, respectively. These ranges align with experimentally assigned IR peaks,[43, 242, 246] even though the calculated frequencies relative to hollow sites seem to be underestimated by roughly 30 cm^{-1} . Additionally, we note a blue shift of CO stretching frequencies with increasing surface coverage, that can be ascribed to strengthening of the C-O bond due to reduced π backdonation from the metal. This observation agrees with the experimentally reported trend of reduced CO activation with increasing coverage.[247] Interestingly, on the (111) and (100) facets increasing surface coverage starts to affect the CO stretching frequencies only from 3/7 and 2/3 ML, respectively, indicating a marginal contribution of lateral interactions to adsorbate stability for the lower coverages.

4.1.3. CO-induced Surface reconstruction

In Figure 4.3 we present snapshots of the free-standing Co NPs with increasing size obtained from our MC simulations in vacuum and in the low X_{CO} scenario ($p_{\text{CO}} = 5\text{ bar}$). It is shown that Co NPs undergo significant surface reconstruction when exposed to CO as highlighted by the overall shape changes from a truncated octahedron to a cuboctahedron for all particles except the 2 nm one. The reconstructed particles expose semi-triangular (111) terraces alternating with large square, stepped regions resembling the (311) facet that culminate with small (100) terraces. The surface regions where the (111) terraces intersect, that are populated by Edge B1 and B5-B sites, are greatly reduced in the reconstructed particles with respect to the pristine ones. With growing size, the surfaces of both the pristine and reconstructed particles become increasingly defective, even though this is more prominent for the former.

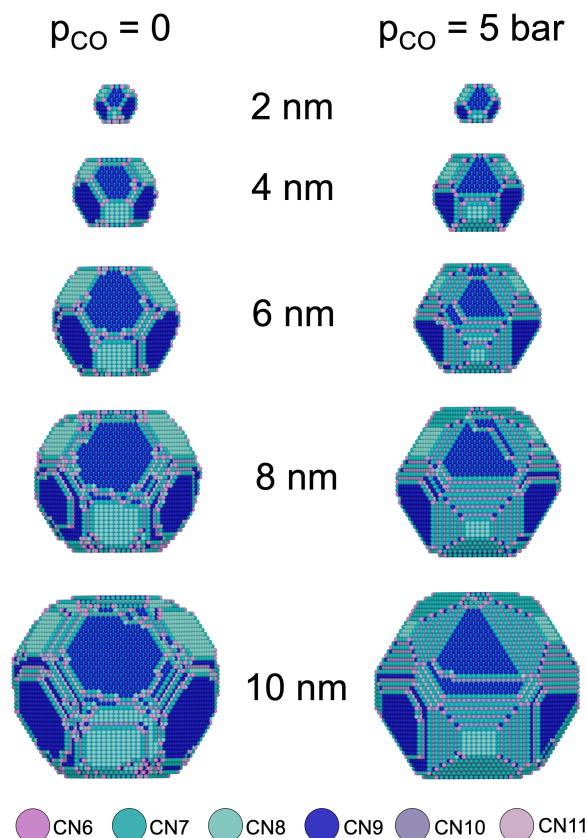


Figure 4.3.: Structural models of Co NPs in the investigated size range in vacuum and exposed to $p_{\text{CO}} = 5$ bar. Reproduced from [240] with permission from the Royal Society of Chemistry.

In Figure 4.4 we present the side views of 8 nm NPs where both the effects of the MSI (for the strongly-interacting CoTiO_3 support) and of p_{CO} are taken into account. With increasing p_{CO} , we observe a gradual transition of the NP from the TO to the cuboctahedral shape, where the surface becomes increasingly more stepped and the (111) terraces evolve from the hexagonal to the triangular conformation. The appearance of triangular (111) terraces arise from the fact that C insertion stabilizes only the B5-A and not the B5-B sites, that do not present a planar fourfold site. Thus, with increasing p_{CO} , the three sides of the hexagonal terraces at the intersection with the (100) facets that contain B5-A sites grow at the expenses of the other three sides at the (111)/(111) intersections that expose B5-B sites instead, causing the overall change in morphology. We note that this prediction is in agreement with previous experimental studies that reported triangular nano-islands formation over Co single crystals upon exposure to a syngas mixture,[237, 239] and to pure CO.[248] These observations were reinforced by theoretical calculations by Banerjee et al.[238] that predicted spontaneous formation of these structures on (111) planes under FT conditions driven by C insertion.

In Figure 4.4, it is evident that CO adsorption causes a rounding of the NP surfaces, a behavior that has also been previously observed for Pt NPs.[249, 250] This leads to a

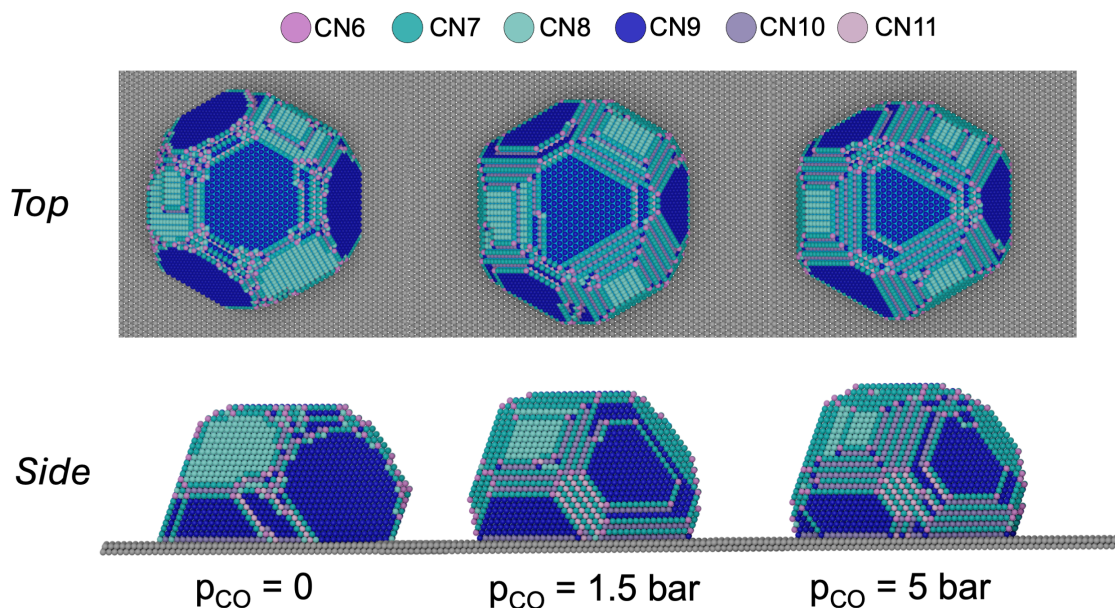


Figure 4.4.: Top and side views of a CoTiO₃-supported 8 nm Co NP in vacuum, in the high X_{CO} ($p_{\text{CO}} = 1.5$ bar) and low X_{CO} ($p_{\text{CO}} = 5$ bar) scenarios. Co atoms are colored based on their CN. Reproduced from [240] with permission from the Royal Society of Chemistry.

decrease in Co dispersion, quantified in Figure 4.5, due to the decrease in surface/volume ratio as the NPs become more spherical. Since in our models, as explained in Section 4.1.1, we employed an effective adhesion energy equal to $\gamma_{\text{adh}} - \Delta G_{\text{ads}}^{(111)}$, increasing p_{CO} results in a reduction of the MSI, that is reflected by the NPs being less flattened on the CoTiO₃ support and reaching heights of 25, 27, and 28 atomic layers in vacuum, at low X_{CO} and high X_{CO} , respectively. According to our calculations, γ_{adh} on the SiO₂ support is lower than $\Delta G_{\text{ads}}^{(111)}$ that implies complete detachment of the NPs from the support. Since this is not reported experimentally, we conclude that either we did not capture the real conformation of the Co-SiO₂ interface, and that the actual one yields stronger adhesion, or that NPs leaching is kinetically hindered under FT conditions. At any rate, by reducing the Co-support interactions, CO is likely to favor particle migration and coalescence.

We now turn to the site distribution analysis of the reconstructed NPs considering the simplified site scheme used in Section 3.1.3, that is shown in Figure 4.6. At first glance, the most striking effect of the CO gas phase is a dramatic increase of B5-A sites concentration at the expenses of the 2B3 and B4 terrace sites. B6 sites are also drastically reduced, resulting in a smoothening of the step edges in the reconstructed particles. In comparison, B5-B sites are mostly unaffected by p_{CO} , due to the fact that even if the intersections where B5-B sites are located become narrower in the (100)/(100) direction, they become wider in the (111)/(111) one. Interestingly, the site distribution for the 2 nm NPs stays roughly the same in the investigated p_{CO} range, which indicates that small particles do not reconstruct as easily as the larger ones. Furthermore, we note that in the X_{CO} regimes the Co NPs reconstruct in the same qualitative fashion, albeit with rather marked quantitative

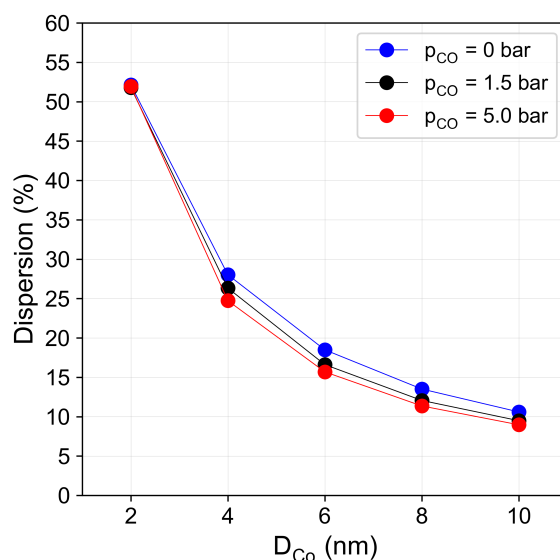


Figure 4.5.: Dispersion (defined as N_{surf}/N_{tot} where N_{tot} and N_{surf} are the total number of atoms and number of surface atoms, respectively) of free-standing Co NPs with increasing D_{Co} and p_{CO} . Error bars have been omitted as they are negligibly small. Reproduced from [240] with permission from the Royal Society of Chemistry.

differences. For the 10 nm NP, for instance, we report a 4.6, 4.9 and 11.4 % differences for the 2B3, B4 and B5-A sites, between the high and low X_{CO} scenarios, indicating that non steady-state regimes that can be expected during FT might considerably affect the surface conformation of Co NPs. Different MSI were once again shown to have a negligible impact on the site distribution (Figures A.5, A.6). To estimate the sensitivity of the models on the energy correction for CN = 10, we carried out further MC simulations in the low X_{CO} scenario considering $\Delta G_{rxn} = 0.32, 0.21$ (i.e., 3/4 and 1/2 of the original correction) and 0 eV, with the resulting site distribution analysis shown in Figure 4.7.

We observe that without considering C insertion in the B5-A sites, Co NPs undergo a different type of surface reconstruction as B5-A sites mostly disappear in favor of B4 and B5-B sites. On the other hand, considering $\Delta G_{rxn} = 0.32$ and 0.21 eV leads to a qualitatively similar reconstruction as compared to the original case of $\Delta G_{rxn} = 0.42$ eV, as in both cases we witness an increase of B5-A sites % with respect to the particles in vacuum. Nonetheless, the extent of the reconstruction changes significantly with ΔG_{rxn} , underscoring that model is rather sensitive to the magnitude of the correction for CN = 10 and the pivotal role of inserted C.

Quantifying the overall effect of surface reconstruction on the TOF of the fcc-Co NPs is not a trivial task and would require an extensive microkinetic model, that is beyond the scope of this work. Nevertheless, we can attempt to qualitatively discuss the most likely scenario based on the observed changes in site distribution and the ΔH_{act} derived in Section 3.2.3. The marked decrease of B6 sites, of which the B6 (641) type was shown to be the most active LCS for direct CO dissociation, suggests a detrimental effect of surface reconstruction on catalyst activity. Nonetheless, it is an open question whether these sites would be present on the Co NPs surfaces in any practical application. Böller

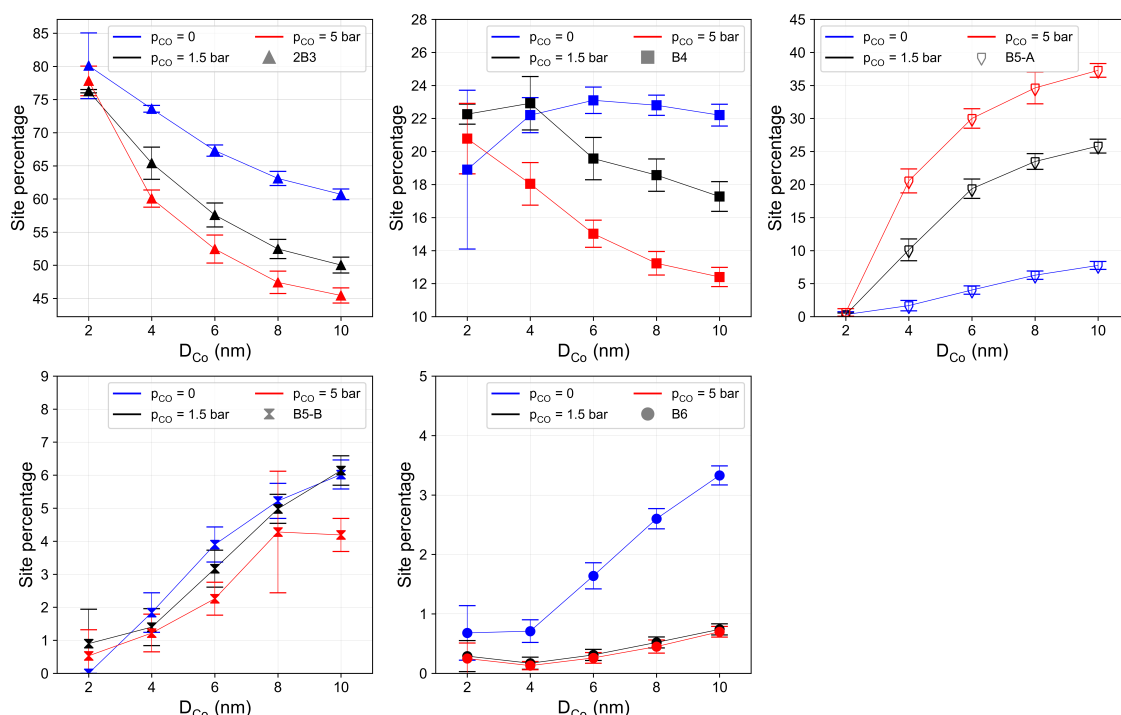


Figure 4.6.: Site distribution analysis with increasing particle size and changing p_{CO} . Reproduced from [240] with permission from the Royal Society of Chemistry.

et al.[178] observed a considerable smoothening of the edges of their Co single crystal, entailing suppression of kink sites, already from a syngas pressure of 1 bar. It is plausible that the elimination of the B6 sites occurs from low p_{CO} and that is rather insensitive to further pressure increase. This hypothesis is supported by the fact that, according to our simulations, the B6 sites percentages are almost identical between the high and low X_{CO} scenario. We additionally speculate that this component of the surface reconstruction, i.e. the smoothening of the step edges, occurs on rather short time scales: the process, in fact, involves CO adsorption and diffusion on the Co surface of the subcarbonyl species, which are not expected to be characterized by high energy barriers. Next in line in terms of activity are the B5-A step sites, that dramatically increase upon reconstruction and whose concentration was found to be rather sensitive to relatively small oscillations of p_{CO} . This component of the reconstruction, on the other hand, is expected to occur on longer time scales, as it is mostly driven by C insertion and thus depends on CO dissociation. To sum up, we speculate that, as soon as the Co NPs are exposed to a CO atmosphere even at low pressures, the NP surface reconstruct to suppress the B6 sites, causing a decrease of the TOF. Once this has taken place, further CO exposure at increasing pressures triggers the second component of the reconstruction, i.e. the drastic increase of step sites, that would result in an increase of the TOF. This picture would align with the frequently observed induction period in the initial stage of the FT synthesis, during which the activity increases before stabilizing at steady-state regime, and that is often ascribed to the time required for the NPs to reconstruct and expose more active sites. [251–254] However, it has proven challenging to confirm experimentally the existence of this beneficial surface

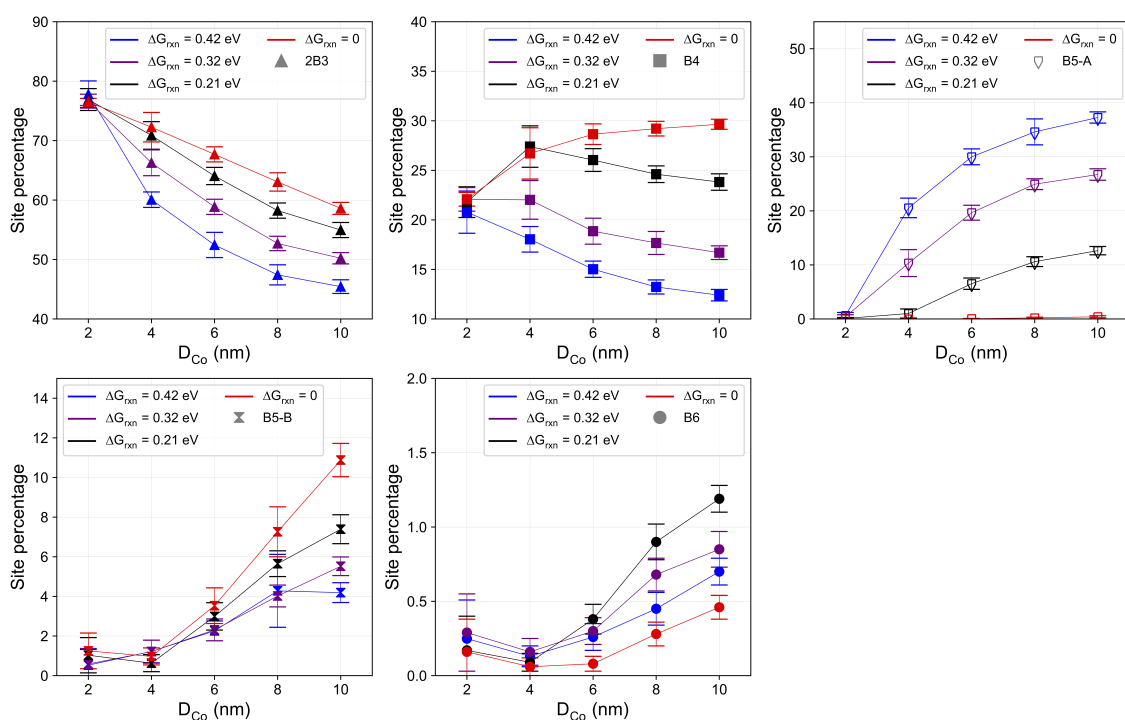


Figure 4.7.: Site distribution analysis with increasing particle size in the low X_{CO} scenario and changing the energy correction ($\Delta G_{rxn}/2$) applied to the Co atoms with CN = 10. Reproduced from [240] with permission from the Royal Society of Chemistry.

reconstruction. Fischer et al. tried to pretreat the catalyst in a pure CO atmosphere to cause surface reconstruction, that was expected to increase activity but that led to substantial deactivation instead.[46] We argue that this was due the lack of H_2 , that prevents the C monomers formed upon CO dissociation from hydrogenating and desorb and thus end up carburizing the catalyst.[76, 90, 255]

Interestingly, we note that the surface concentration profile of the B5-A sites in the typical high X_{CO} scenario somewhat mirrors the experimental structure-sensitivity trends, as they increase roughly linearly upto $D_{Co} = 6$ nm, and approach a plateau afterwards, in line with the structure insensitivity of Co NPs for $D_{Co} > 10$ nm. Despite their very low concentration, however, B6 sites likely play a role in the determination of the TOF since they can have CO dissociation barriers ~ 0.2 eV lower than the predominant B5-A (311) sites, that corresponds to roughly a x100 difference in reaction rate. Nevertheless, we stress that these are more qualitative hypothesis, as a comprehensive microkinetic model (considering realistic coverages) also including the hcp-Co phase would be necessary to draw quantitative conclusions. To conclude this section, we note that different studies on Co single crystals that tried to unravel surface reconstruction under a CO or syngas gas phase have obtained contradicting results.[178, 237, 239, 256, 257] Single crystals, however, might behave differently from NPs and the pressures considered in these works are typically lower than those at which industrial FT is carried out. Bezemer et al.[42] reported surface reconstruction of Co NPs under FT conditions based on a reduction of Co atoms CN as measured by EXAFS, that aligns with increase of step sites reported

here. A further study that supports this hypothesis is one by Prieto et al.[43], where the appearance of bands located at lower frequencies in their IR spectra was once again ascribed to the decrease of Co atoms CN. Other theoretical studies have applied the Wulff construction to predict the shape of Co NPs under a CO atmosphere, which was found to expose more close-packed surfaces at the expenses of the stepped ones with respect to the particles in vacuum, in contrast to the trend reported here. This might be motivated by the shortcomings of the Wulff construction listed in Section 3.1.3 as well as by the fact that C insertion was not considered in these studies.[258–260]

Although the CO-induced surface reconstruction of Co catalysts was proposed several decades ago, it remains a subject of ongoing debate. This is largely due to the challenges associated with obtaining experimental evidence that can unequivocally confirm this phenomenon under industrial FT conditions. In such environments, high pressures and substantial wax formation significantly complicate the application of many experimental techniques. In this context, a theoretical approach can provide valuable insights, as it allows the effects of individual factors to be disentangled, ultimately enabling a simplified description of an otherwise highly complex chemical system.

4.1.4. Energetics of Co NPs in a CO Gas Phase

Co adsorption also has a considerable effect on the energetics of Co NPs. This is shown in Figure 4.8, where we report the γ , average energy per atom (ΔE_{Co}) and chemical potential ($\Delta \mu_{Co}$) of the free-standing Co NPs with increasing p_{CO} . The results for the supported particles are given in Figures A.7, A.8. Notwithstanding the higher number of LCS on the reconstructed particles, we observe in Figure 4.8a that γ decreases drastically by roughly 40% and 45% for $p_{CO} = 1.5$ and 5 bar, respectively. We can link this result to the observation by several experimental studies of further reduction of the catalyst during FT.[87, 261–263] In fact, the reduction, or lack thereof, of Co NPs is mainly determined by the balance between γ of Co^0 and $Co(II)O$: bulk Co^0 is more stable than the oxide under typical reduction or FT conditions, but the latter is characterized by a lower surface energy. As the particles become smaller, and their surface/volume ratio increases, reduction becomes increasingly less favorable causing the persistence of some CoO species in the catalyst after reduction. This is the case for Co but also, for instance, for Ni.[82, 264] Due to the decrease of γ upon CO adsorption, small particles that did not reduce after activation might hence do so when put into FT operation. Furthermore, we note that the reduction of γ with increasing D_{Co} is less pronounced in the presence of CO with respect to vacuum, as in the former case it amounts to $\sim 15 \text{ meV}/\text{\AA}^2$ between the 2 and the 10 nm particles while in the latter the difference is $24 \text{ meV}/\text{\AA}^2$.

As illustrated in Figure 4.8b, an increase in p_{CO} also leads to a reduction of ΔE_{Co} , which we attribute to two concurrent effects. First, as shown in Figure 4.8a, exposure to CO decreases the surface energy γ of Co NPs. Second, Co NPs in a CO atmosphere exhibit a reduced surface-to-volume ratio, as evidenced by the dispersion versus D_{Co} plot in Figure 4.5, since surface corrugation promotes the adoption of a more rounded morphology. We further observe that the dependence of ΔE_{Co} on p_{CO} is non-linear: increasing p_{CO} from 0

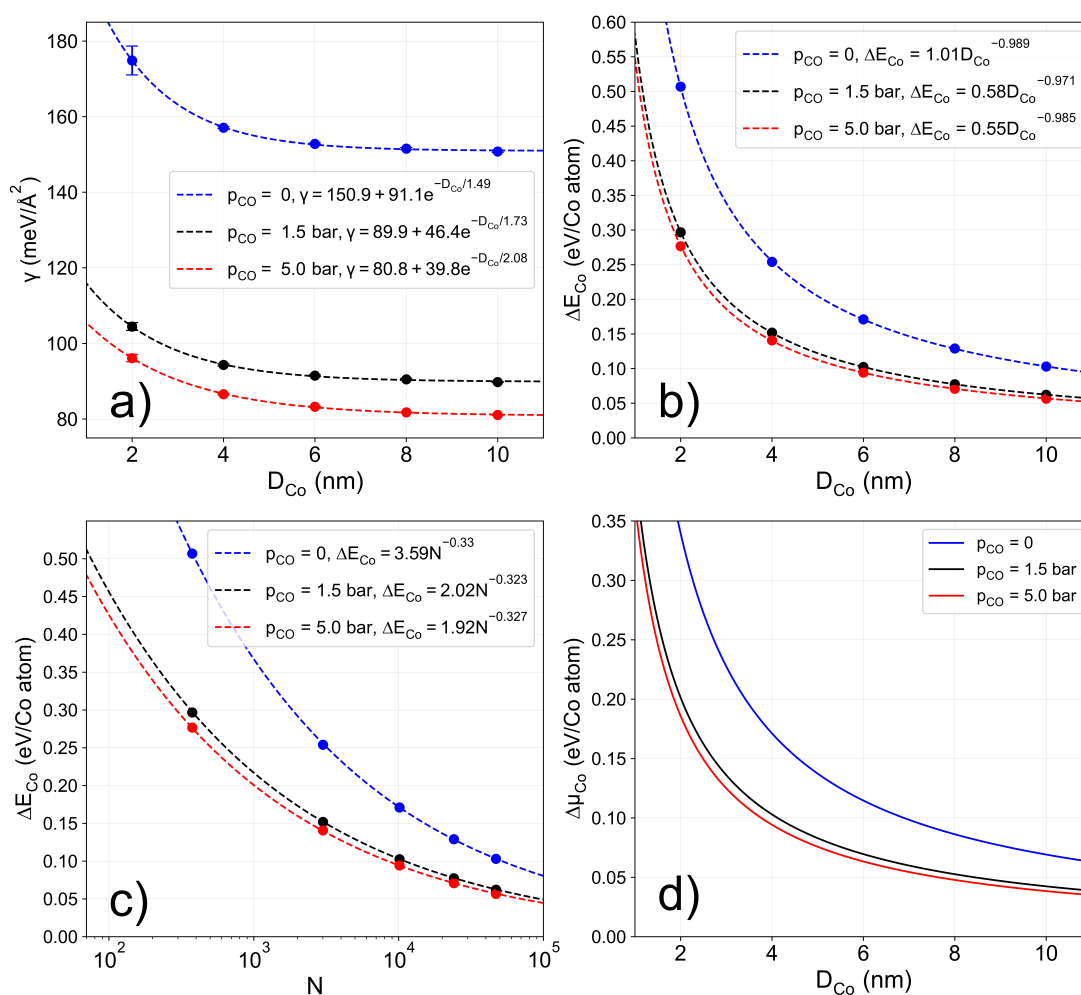


Figure 4.8.: Free-standing Co NPs a) surface energies with increasing D_{Co} and p_{CO} , b) average energy per atom ΔE_{Co} with respect to bulk Co with increasing D_{Co} and p_{CO} and c) with increasing number of atoms (N) and p_{CO} . d) Chemical potential of the free-standing Co NPs with respect to bulk Co $\Delta \mu_{Co}$ with increasing D_{Co} and p_{CO} . Reproduced from [240] with permission from the Royal Society of Chemistry.

to 1.5 bar results in a pronounced decrease in ΔE_{Co} , whereas a further increase to $p_{CO} = 5$ bar leads to only a minor additional reduction. This behavior arises from the logarithmic dependence of ΔG_{ads} on p_{CO} , which translates into a relatively weak sensitivity of ΔE_{Co} to variations in p_{CO} within the range relevant to FT synthesis. Accordingly, we conclude that under operating conditions, the overall thermodynamic stability of Co NPs is not expected to be significantly influenced by fluctuations of p_{CO} in the 1–10 bar range.

The considerations made for ΔE_{Co} , are also valid for $\Delta \mu_{Co}$, that is shown in Figure 4.8d. We find that the $\Delta \mu_{Co}$ curves become markedly less steep in the presence of CO. Specifically, the decrease of $\Delta \mu_{Co}$ with D_{Co} over the 2–10 nm size range amounts to approximately 0.16 eV/atom under CO atmosphere, compared to 0.29 eV/atom for particles in vacuum. Because CO primarily affects NP stability by reducing their surface energy, it stabilizes smaller particles more strongly than larger ones, owing to their higher surface-to-volume ratio. As a result, CO lowers the thermodynamic driving force for sintering of Co NPs.

Importantly, however, the presence of CO significantly accelerates the sintering kinetics, an hypothesis that will be demonstrated in Section 4.2. As previously discussed, CO reduces the adhesion energy of Co NPs on the support, facilitating their migration and coalescence. In addition, increasing p_{CO} promotes the formation of Co subcarbonyl species, which are believed to drive sintering via Ostwald ripening.[71, 72, 74, 200] Extensive experimental studies of $\gamma\text{-Al}_2\text{O}_3$ -supported Co catalysts under operating conditions have indeed shown that higher p_{CO} enhances sintering,[71] indicating that the increase in sintering kinetics offsets the reduced thermodynamic driving force.

Overall, through the case study of CO adsorption on Co NPs, this section demonstrates that the gas-phase environment can exert a substantial influence on NP stability. This highlights the importance of accounting for adsorbate effects when modeling stability-dependent phenomena—such as sintering, metal reoxidation, and encapsulation by the support—which can be straightforwardly incorporated within the framework of our DFT-MC model.

4.1.5. Conclusions

In this section, we have refined our DFT-MC approach to take into account the effect of adsorbates, that was demonstrated considering CO adsorption on Co FT catalysts as case study. The effect of CO was considered implicitly in the MC simulations by applying CN-specific energy corrections derived from DFT adsorption energy calculations on periodic models. Even though there might be some irregular regions on the Co NPs surface where the model fails to accurately capture the adsorption energetics, these are likely negligible considering the large sizes of the systems considered here. On the other hand, this approach enormously simplifies our task and enables us to simulate an ensemble of NPs with tens of thousand of atoms, considering simultaneously the effects of the support and of the gas phase, in just a few days. The outcomes of our simulations revealed that the FT gas phase drastically alters the structures of fcc-Co NPs: we observed a bimodal surface reconstruction that entails on the one hand a smoothening of the step edges, with consequent suppression of B6 sites, and on the other a drastic increase of the stepped regions found at the (111)/(100) intersections exposing B5-A sites. Furthermore, CO adsorption significantly reduces the surface energy of Co NPs, profoundly altering the $\Delta\mu_{\text{Co}} - D_{\text{Co}}$ profiles. These will be invoked in the following section, where we simulate the Ostwald ripening of Co NPs under industrially relevant time scales and show that CO considerably affects also catalyst deactivation.

4.2. Sintering Simulations of Co NPs during FT

4.2.1. Introduction and Methods

Scope. Besides influencing the Co NPs structures and energetics, CO also significantly affects the stability of the catalyst. In particular, increasing p_{CO} has been shown to drastically accelerate sintering, that is believed to occur via support-mediated Ostwald ripening.[71, 72, 74] In this context, it has been postulated that the role of CO is to form mobile Co subcarbonyl species that, by diffusing on the support, cause a net mass flux from the small particles to the larger ones that leads to a loss of active surface.

In this section, we carried out support-mediated Ostwald ripening simulations to investigate the effects of p_{CO} and initial particle size distribution on the deactivation rate of fcc-Co catalysts supported on γ - Al_2O_3 and both rutile and anatase TiO_2 . The simulations are based on an analytical model where all the necessary quantities but one are derived *ab initio*. Our results reveal that due to the high CO content of the subcarbonyl species, relatively small p_{CO} changes significantly affect the sintering process. The initial average D_{Co} also has a rather large effect on the sintering, with smaller D_{Co} enhancing deactivation. The initial width of the particle size distribution can have an effect on when the deactivation kicks in, but it is comparatively small with respect to the other factors considered.

Methods. All the DFT calculations were carried out with the same settings as described in the previous sections. The TS searches in the calculations of the diffusion paths were carried out with the climbing image (CI) nudged elastic band (NEB) method,[265, 266] using three images in between the initial and the final state. When the PES of the TS was found to be particularly shallow, a further CI-NEB calculation was carried out in between the two high-lying images previously identified.

The starting point of the sintering simulations is a normal distribution of 500 Co NPs, whose size evolution is determined by the following differential equation:

$$\frac{dR}{dt} = \frac{XY}{X+Y} \frac{K}{R^2} \exp\left\{\left[\frac{-\Delta G_{tot}}{kT}\right]\right\} \left(\exp\left\{\left[\frac{\Delta\mu_{NP}(R^*)}{kT}\right]\right\} - \exp\left\{\left[\frac{\Delta\mu_{NP}(R)}{kT}\right]\right\} \right) \quad (4.3)$$

where:

$$K = \frac{v_s \Omega}{4\pi a_0^2 \alpha_1} \quad (4.4)$$

$$X = 2\pi a_0 R \sin \alpha \quad (4.5)$$

$$Y = \frac{2\pi a_0^2}{\ln [L/(R \sin \alpha)]} \quad (4.6)$$

In the above equations:

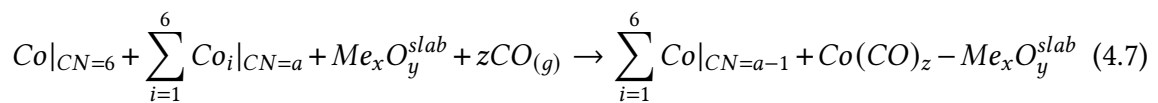
- R is the curvature radius of the NPs;
- ΔG_{tot} is the sum of $\Delta G_{form} + \Delta G_{diff}$, that are the subcarbonyl species Gibbs free energy of formation on the support and diffusion barrier, respectively. For a given support, the employed diffusion barrier was the lower between those in the x and y direction;
- R^* is the critical radius in the NPs ensemble, i.e. the radius of the particles that, at a given instant, are neither shrinking nor growing;
- ν_s is the vibrational frequency of the subcarbonyl species on the support;
- Ω is the molar volume of Co;
- a_0 is the lateral lattice constant of the support;
- α is the contact angle at the NP-support interface;
- α_1 is equal to $[2 - 3 \cos \alpha + \cos^3 \alpha]/4$;
- L is the diffusion length for the subcarbonyl concentration to reach its far field limit.

Pioneering work regarding the mechanistic aspects of Ostwald ripening was carried out by Wynblatt and Gjostein[267], while the above rate equation was elaborated and adapted to the case of migrating metal-adsorbate complexes in more recent works by Parker [268] and Ouyang.[200] In this work, all quantities in Equations 4.3,4.4,4.5 and 4.7 but one were derived *ab initio*. E_{tot} and ν_s were calculated via DFT, the $\Delta\mu_{NP}(R)$ profiles and α (here taken as the average between the two NP-support contact angles, i.e. 118°) were obtained from the outcomes of the MC simulations in Section 4.1 and the remaining parameters are easily deducted from the geometries of fcc-Co and of the support slabs. L , the only parameter we could not derive, was always assumed as 20 nm.

We employed a time step of 1 s, and each simulation covered a time span of four weeks. Particles that, throughout the simulations, became smaller than 0.5 nm were filtered out of the ensemble and were thus considered as disintegrated. As previously outlined,[202] there is no unique definition of R^* that ensures that the initial total mass is conserved over the simulation length. Thus, as it was done in a previous work,[201] the R^* was determined numerically at each step via a bisection method that enforces mass conservation.

4.2.2. Co Subcarbonyls Formation and Diffusion Energies

Co subcarbonyl formation energies. Considering that the lowest-coordinated atoms, and hence those that detach more easily from the Co surface, in our MC NPs had a CN = 6, the formation of the Co subcarbonyl species was modeled according to the following reaction:



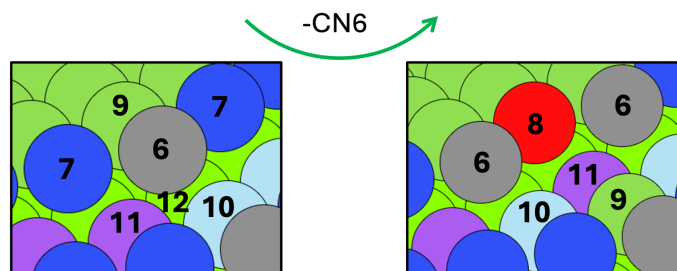


Figure 4.9.: The coordination environment of the detaching Co atom with CN = 6. The numbers written on the atoms represent their CN.

Where $Co|_{CN=6}$ is the detaching Co atom, Co_i is its i^{th} neighbor, $Me_xO_y^{slab}$ is the support slab and $Co(CO)_z - Me_xO_y^{slab}$ is the subcarbonyl species adsorbed on the support slab. The generic coordination environment of the Co atom with CN = 6 was modeled as highlighted in Figure 4.9.

The energies of the Co atoms with different CN were taken from the energy model of Figure 4.2. We note that the energy difference between the left and right configurations in Figure 4.9 is 4.54 and 4.52 eV in the low and high X_{CO} scenarios, respectively. The calculated ΔG_{form} of $Co(CO)_x$ ($x = 1-3$) species and ν_s on the different supports investigated are given in Table 4.2.

Table 4.2.: Gibbs free energies of formation ΔG_{form} and vibrational frequencies (reported only for the most stable subcarbonyl species) of $Co(CO)_x$ ($x = 1-3$) on different supports. For each $Co(CO)_x$ on each support, only the data for the most stable adsorption site on the support slab are given.

Support	$Co(CO)_x$	ΔG^f (eV)		ν_s (s^{-1})
		$p_{CO} = 1.5$ bar	$p_{CO} = 5.0$ bar	
γ - Al_2O_3 (110)	$Co(CO)$	1.38	1.33	–
	$Co(CO)_2$	1.47	1.42	–
	$Co(CO)_3$	1.06	0.92	4.04×10^{12}
Rutile TiO_2 (110)	$Co(CO)$	1.13	1.08	–
	$Co(CO)_2$	0.96	0.87	6.28×10^{12}
	$Co(CO)_3$	1.16	1.02	–
Anatase TiO_2 (101)	$Co(CO)$	1.33	1.28	–
	$Co(CO)_2$	1.13	1.04	–
	$Co(CO)_3$	0.98	0.84	5.33×10^{12}

γ - Al_2O_3 (110). The PES of $Co(CO)_3$ on the support slab is presented in Figure 4.12. Here, we considered an hydration degree of 3 H_2O molecules per unit cell, that results in a OH groups density of 8.9 OH/nm². It is found that the strongest adsorption site is on a unterminated O, but the subcarbonyl hops on different surface hydroxyl groups along its

diffusion path, where it is also rather stable. The minimum energy diffusion path is in the x direction, with a diffusion barrier of 0.54 eV.

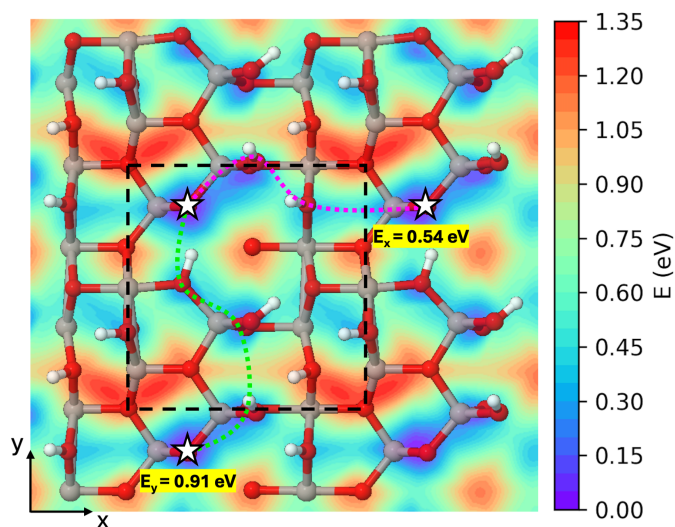


Figure 4.10.: The potential energy surface (PES) of $\text{Co}(\text{CO})_3$ on the hydrated (8.9 OH/nm^2) $\gamma\text{-Al}_2\text{O}_3$ (110) facet.

Anatase TiO_2 (101). The migrating species is once again $\text{Co}(\text{CO})_3$, that diffuses hopping from one dangling O to the other. Diffusion barriers were found to be the same in the x and y direction and lower to that reported for $\text{Co}(\text{CO})_3$ on $\gamma\text{-Al}_2\text{O}_3$ (110), amounting to 0.44 eV.

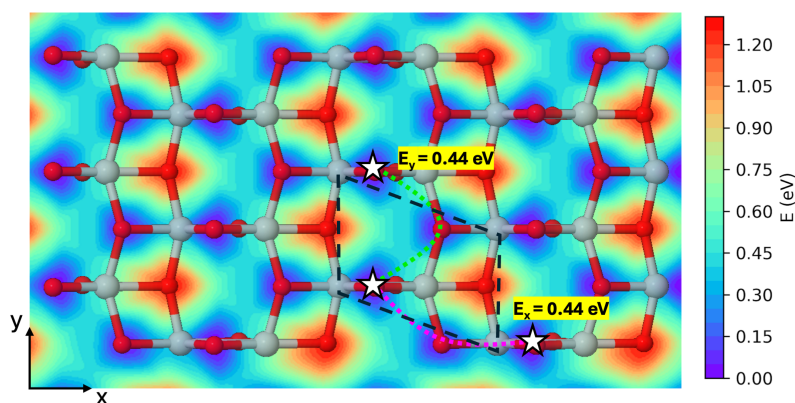


Figure 4.11.: The potential energy surface (PES) of $\text{Co}(\text{CO})_3$ on the stoichiometric anatase TiO_2 (101) facet.

Rutile TiO_2 (110). This is the only support where the bidentate subcarbonyl was found to be more stable than $\text{Co}(\text{CO})_3$. The most stable adsorption site is one where the subcarbonyl binds to two dangling O simultaneously, and the diffusion path in the y direction is much more favourable than in the x direction, with barriers of 0.42 and 1.05 eV, respectively.

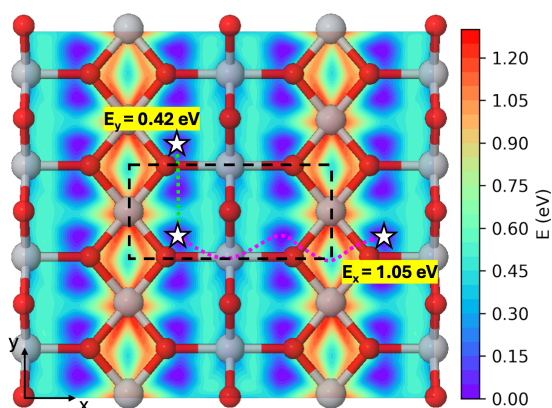


Figure 4.12.: The potential energy surface (PES) of $\text{Co}(\text{CO})_2$ on the stoichiometric rutile TiO_2 (110) facet.

4.2.3. Ostwald Ripening Simulations

Effect of CO partial pressure. The particle size distribution of the $\gamma\text{-Al}_2\text{O}_3$ -supported Co NPs (Figure 4.13a) is largely unaffected when the catalyst is exposed to a $p_{\text{CO}} = 1.5$ bar, which is also clearly visible by the solid lines in Figure 4.13c that indicate barely any change in terms of dispersions, number of particles as well as average D_{Co} . Under a $p_{\text{CO}} = 5$ bar gas phase, however, the particle size distribution (Figure 4.13b) visibly changes throughout the simulation, as it is shown to progressively drop due to particles disintegration and to shift towards larger D_{Co} .

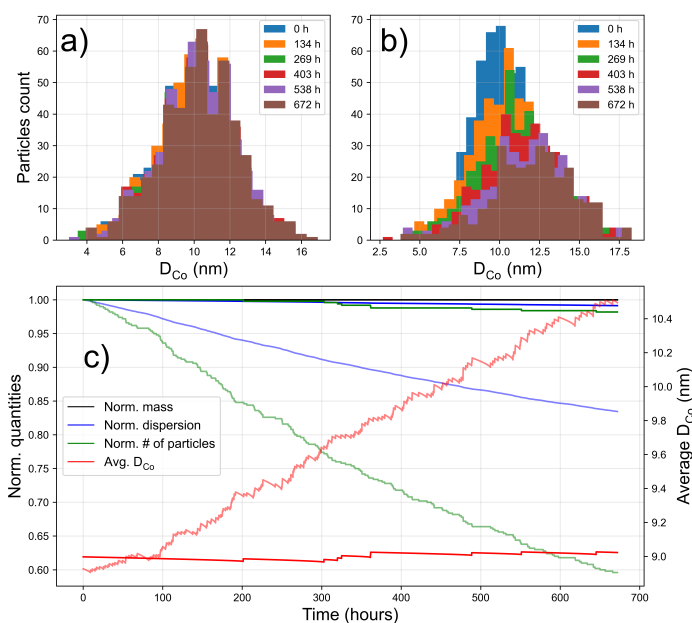


Figure 4.13.: Evolution of a normal distribution ($\sigma = 20\%$) of 500 Co NPs supported on $\gamma\text{-Al}_2\text{O}_3$ (110) with a) $p_{\text{CO}} = 1.5$ bar and b) $p_{\text{CO}} = 5$ bar. Relevant quantities are reported in c), where the solid and shaded lines correspond to $p_{\text{CO}} = 1.5$ and 5 bar, respectively.

Additionally, the asymmetric shape of the final distribution (672 h) is typical of catalysts that underwent sintering via Ostwald ripening, with a long tail of small particles preceding the main distribution peak. As shown by the faded lines in Figure 4.13c, the dispersion and number of particles decrease while the average D_{Co} increases linearly with time. The marked differences between the two scenarios originates from the change of ΔG_{form} , that goes from 1.06 to 0.92 eV when p_{CO} increases from 1.5 to 5 bar. While the energy difference might appear small, at FT temperatures of 500 K this results in roughly x30 rate speedup, causing relatively small p_{CO} variations to drastically affect the process. Nonetheless, even at $p_{CO} = 5$ bar, the sintering rate is moderate, with a loss of dispersion of only $\sim 15\%$ over a period of four weeks.

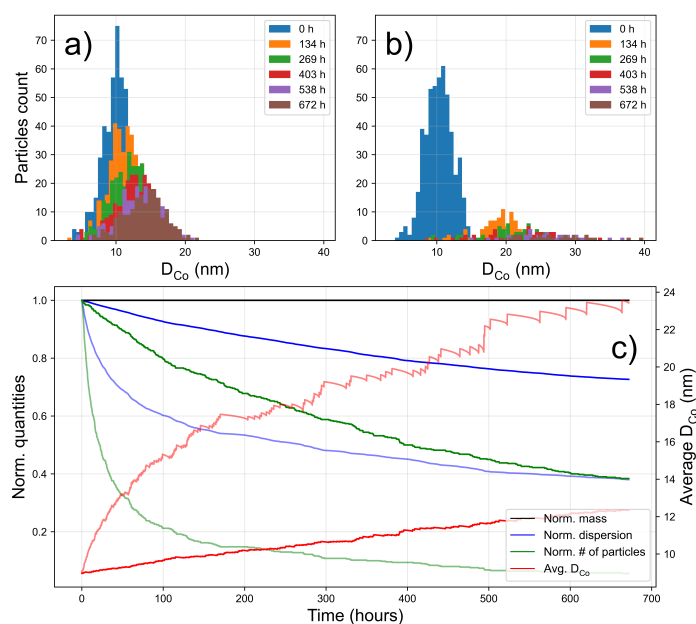


Figure 4.14.: Evolution of a normal distribution ($\sigma = 20\%$) of 500 Co NPs supported on anatase TiO_2 (101) with a) $p_{CO} = 1.5$ bar and b) $p_{CO} = 5$ bar. Relevant quantities are reported in c), where the solid and shaded lines correspond to $p_{CO} = 1.5$ and 5 bar, respectively.

The lower ΔG_{form} and ΔG_{diff} on the anatase support cause a considerable increase in sintering rates (Figure 4.14): by the end of the simulation, we witness roughly a 25% loss of surface area with 60% of the particles having disappeared for $p_{CO} = 1.5$ bar, while a surface area loss of 60% accompanied by disintegration of more than 95% of the initial particles is observed for $p_{CO} = 5$ bar. In the low X_{CO} (i.e. high p_{CO}) scenario, we observe very fast sintering within the first 100 hours, which slows down later on. This is attributed to the progressive decrease of the thermodynamic driving force, due to the flattening of the $\Delta\mu_{Co}$ profile (Figure 4.8d), as the particles grow bigger. In particular, sintering significantly slows down once the average D_{Co} of the ensemble reaches ~ 15 nm.

The simulations for the rutile TiO_2 support, whose outcomes are displayed in Figure 4.15, yield similar results with respect to those for anatase. We note, however, that the impact of p_{CO} is mildly reduced in comparison to the previous case because, due to its lower CO content, the formation energy of the bidentate subcarbonyl is less affected by p_{CO} . This

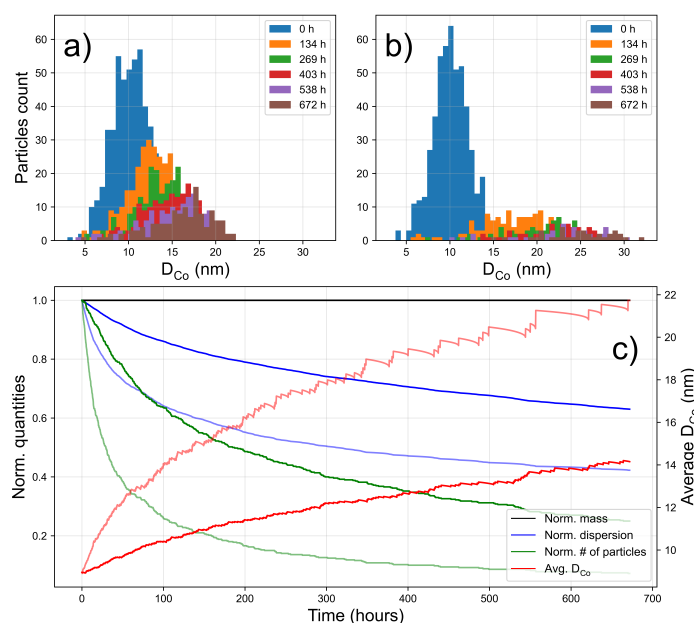


Figure 4.15.: Evolution of a normal distribution ($\sigma = 20\%$) of 500 Co NPs supported on rutile TiO_2 (110) with a) $p_{\text{CO}} = 1.5$ bar and b) $p_{\text{CO}} = 5$ bar. Relevant quantities are reported in c), where the solid and shaded lines correspond to $p_{\text{CO}} = 1.5$ and 5 bar, respectively.

underscores that the sintering response to changes in p_{CO} depends on the nature of the diffusing subcarbonyl species.

Effect of mean initial D_{Co} . As highlighted in Figure 4.16, the mean initial D_{Co} can also have a prominent effect on the sintering kinetics. On the $\gamma\text{-Al}_2\text{O}_3$ support at $p_{\text{CO}} = 5$ bar, decreasing particle size causes the NPs to sinter more rapidly, with a final loss of surface area of 55, 27 and 17% for mean initial $D_{\text{Co}} = 4, 7$ and 9 nm, respectively. The importance of this effect depends on the derivative of $\Delta\mu_{\text{Co}}$ with respect to D_{Co} in the vicinity of the mean initial D_{Co} and is greater for the small particles, for which the $\Delta\mu_{\text{Co}}$ profile is rather steep. Additionally, the sintering rate is initially much faster for the distribution centered at $D_{\text{Co}} = 4$ nm, but slows down significantly over time due to the fast growth of the NPs and. By the end of the simulation, the different curves in Figure 4.16 across the different distributions are characterized by similar slopes, indicating similar deactivation rates.

Effect of initial distribution width. Another feature of the initial particle size distribution that affects the sintering process is its width, which here we express as the standard deviation (σ) of the normal distribution. As seen in Figure 4.17, σ mostly seems to determine when the sintering starts to take effect, with narrower distributions showing a delay in the start of the deactivation. This effect, however, is comparatively small with respect to those listed before and might become relevant for narrow initial distributions with $\sigma < 10\%$, even though it is not trivial to achieve this experimentally.

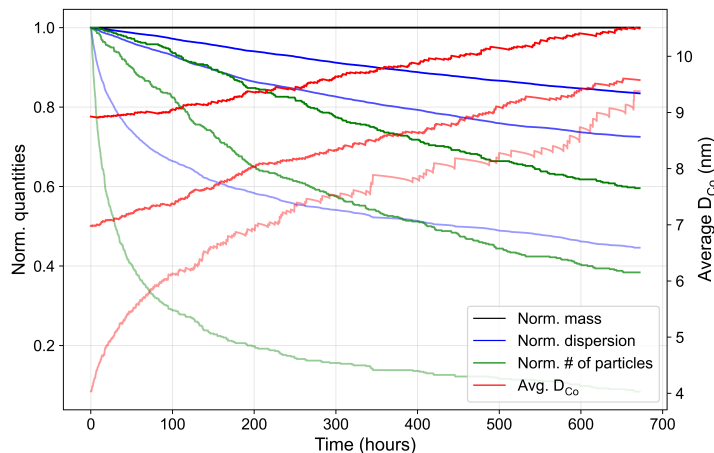


Figure 4.16.: Evolution of relevant quantities throughout sintering simulations at $p_{CO} = 5$ bar of $\gamma\text{-Al}_2\text{O}_3$ -supported normal distributions ($\sigma = 20\%$) of 500 Co NPs centered around (with decreasing fading) $D_{Co} = 4, 7, 9$ nm.

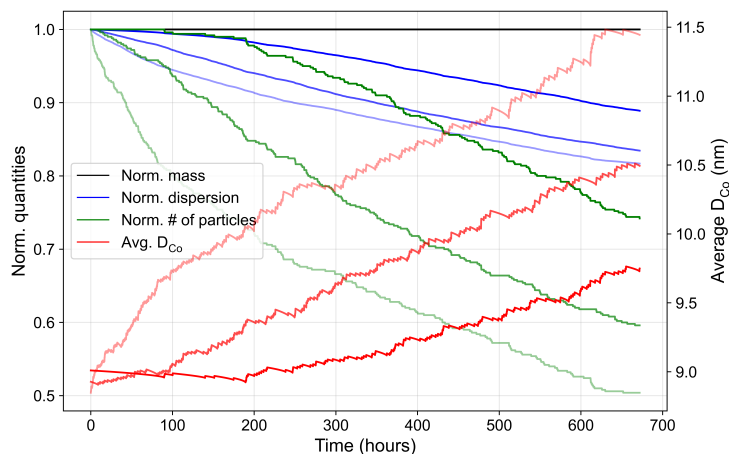


Figure 4.17.: Evolution of relevant quantities throughout sintering simulations at $p_{CO} = 5$ bar of $\gamma\text{-Al}_2\text{O}_3$ -supported normal distributions of 500 Co NPs centered around $D_{Co} = 9$ nm and (with increasing fading) $\sigma = 10, 20$ and 30% .

4.2.4. Conclusions

In this section, we have employed the outcomes of our MC simulations in conjunction with DFT-calculated Co subcarbonyl formation and diffusion energies to carry out Ostwald ripening simulations at industrially-relevant time scales. Due to the relatively low temperature at which the process takes place, small variations of ΔG_{tot} drastically affect the sintering rate. Accordingly, the most important factors influencing the sintering kinetics are p_{CO} and the choice of the support, the first because it affects ΔG_{form} , while the second because it affects both ΔG_{form} and ΔG_{tot} . While we cannot extensively rely on the absolute

sintering rates derived here due to the uncertainty of the DFT calculations of ΔG_{tot} , we can soundly state that reasonable p_{CO} oscillations within the FT range significantly affect the deactivation. Due to the high CO content of the subcarbonyl species, in fact, changes in p_{CO} of a few bar can affect ΔG_{form} to an extent that results in x5-50 differences in sintering rate. This implies that non steady-state conditions, e.g. during plant startup or trips, can significantly speed up catalyst deactivation when they cause a drop in X_{CO} . In comparison, the properties of the initial size distribution were shown to have little effect on NPs sintering, unless the catalyst presents very small initial mean D_{Co} ($< 5-6$ nm). At any rate, this is generally avoided in FT both for the low resulting catalyst activity and proneness to reoxidation of the small particles.

Besides explaining structure-sensitivity and stability trends, here we have demonstrated how the outcomes of the DFT-MC modeling of metal NPs can be used to describe deactivation by Ostwald ripening, a process that largely affects catalyst performance and that is taken in great consideration during catalyst design. Importantly, the model is almost full *ab initio*, and we argue that the estimation of particles energetics is more advanced with respect to what is typically done, as it takes into account the non ideality of the NP shapes, the CO gas phase and the MSI. To conclude, we believe this demonstrates the considerable enhancement of predictive power unlocked by the modeling strategy developed in this thesis.

5. Mn Promotion of Co Fischer-Tropsch Catalysts

Up until this point, we have managed to sketch a comprehensive picture of fcc-Co NPs by probing their structures, reactivity and stability under FT conditions. In this chapter, that closes the results presented in this thesis, we add a final layer of complexity by considering Mn decoration of Co NPs. Given the (just recently) secular history of the FT synthesis and accompanying research focus, it might sound surprising that there are still aspects of catalyst design that can be improved. Yet, fine-tuning Co catalyst properties via addition of other elements is currently a flourishing research area. In this context, the most promising route to deliver the next generation of Co FT catalysts is probably Mn promotion, which we aim to investigate in this chapter.

In the first section, we benchmark our DFT approach against experimental data to ensure that we correctly describe the reactivity of Mn oxides, and additionally derive correlations between formal Mn oxidation state and both its Bader charge and atomic magnetic moment (magmom). In the second, we use our previously derived Co NPs models as slabs in an MLP-powered GA to predict low-energy structures of Mn, from which we derive relevant stability trends and characterize the promoter structures in detail. In the last section, we elucidate the electronic promotion of Mn by calculating reaction paths on a Mn@Co(0001) model, where the simulation setup was elaborated to mirror surface science experiments on Co(0001) single crystals carried out by our collaborators at Helmholtz Zentrum Berlin (HZB).

5.1. Mn Oxides Benchmark

5.1.1. Introduction and Methods

Scope. The accuracy of the predictions in theoretical catalysis depends mostly on the correct estimation of energy differences. These, however, can be hard to achieve with DFT when strongly-correlated systems, such as TM oxides, are under scrutiny. Notoriously, this is due to the failure of the approximate treatment of electron exchange within the DFT formalism to completely cancel the self-interaction error (SIE), that causes electrons in spatially confined orbitals (d and f) to wrongly delocalize. A computationally inexpensive approach to mitigate this shortcoming is the DFT+U method, that introduces via the

parameter U_{eff} an energy penalty for fractional orbital occupations, thereby favoring electron localization.[142, 269–272]

It has been previously reported that predictions of oxygen vacancy formation[273–278] as well as adsorption energies[279–282] are sensitive to the choice of U_{eff} , which hence can largely affect the description of the reactivity of TM oxides. Nonetheless, the magnitude of this correction must be determined case by case, and its choice is often not trivial as no single U_{eff} value can reproduce correctly all the properties of a material. Previous works [283, 284] underscored that, for catalysis applications, the correct representation of redox reactions might be a relevant aspect to consider. Thus, in the first part of this section, we calibrated U_{eff} to match the experimental standard reaction enthalpies (ΔH_{rxn}^0) of MnO oxidation to its higher oxides, i.e. Mn_3O_4 , Mn_2O_3 and MnO_2 . We found that while ΔH_{rxn}^0 strongly depends on U_{eff} , a single value reconciles theoretical predictions with experimental data for all the investigated reactions.

In the second part of this section, we focus on resolving the relations between the oxidation state of Mn and two quantities that can be derived from theoretical calculations, namely the Mn Bader charges and atomic magmoms. While the Mn oxidation state in bulk compounds can be directly inferred from the stoichiometry, binding to the metal surface complicates the picture for Mn oxide structures adsorbed on Co, that we aim to investigate in this chapter. Charge transfer from/to the Co surface, in fact, could cause the experimentally measured Mn oxidation state to deviate from the one that would be expected purely based on cluster stoichiometry. Thus, it is necessary to bridge Mn oxidation state to quantities that can be computed via DFT in order to align theoretical models with experimental measurements.

Herein, this issue was addressed by calculating Mn magmoms and Bader charges for bulk Mn oxides and several gas-phase $\text{Mn}_x\text{O}_y\text{H}_z$ molecules with oxidation states ranging between +1 and +7 that yielded relevant correlations. We found that the magmom-oxidation state correlation was well described by a quadratic fit, that holds true both for bulk and molecular structures. On the other hand, that on the Bader charges was more uncertain, as the data points for the two classes of compounds seemingly lie on two different trend lines with similar slope but shifted among each other.

The results presented in this section are adapted from the following submitted publication:

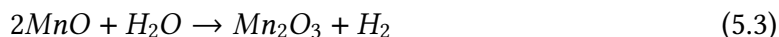
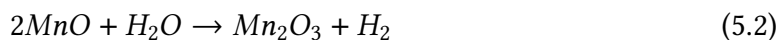
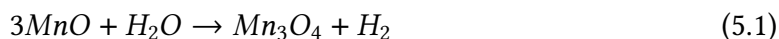
Hoffman, J.-A.; **Sireci, E.**; Gambu, T.; Sharapa, D. I.; Studt, F.; van Steen, E. Bridging Calculated Charges and Formal Oxidation State of Manganese Oxides: A DFT/DFT+U Study. *Physical Chemistry Chemical Physics* **2026**, 28 (27), 17025–17033.

The author especially acknowledges the work carried out by MSc. **Julie-Ann Hoffman** under the supervision of Dr. Thobani Gambu and Prof. Eric van Steen, who calculated the Mn bader charges in the different structures investigated and derived the correlation linking them with the Mn formal oxidation state, in addition to producing Figures 5.1 and 5.3.

Methods. We have employed the same DFT settings as outlined in the previous chapters. Thermal corrections were applied both to the gas-phase molecules and the investigated solids. We calculated the phonons of the investigated bulk structures, that were treated within the harmonic approximation, using the python package Phonopy.[285, 286] We employed 1x1x1, 2x2x1, 1x1x1 and 3x3x4 supercells for MnO, Mn₃O₄, Mn₂O₃ and MnO₂, respectively. Atomic forces were calculated via the finite displacement method with displacement distance of 0.01 Å. The number of resulting displacements, that depends on the symmetry of the crystals, were 4, 21, 60 and 6 for MnO, Mn₃O₄, Mn₂O₃ and MnO₂, respectively. All the phonons calculations were carried out using $U_{\text{eff}} = 0$. ZPEs, $\Delta\Delta H^{0 \rightarrow 298K}$ and standard vibrational entropies (S_{vib}^0) for the different bulk Mn oxides are reported in Table A.5 and compared with experimental standard entropies. Here, we refer to ΔH_{rxn}^0 to determine U_{eff} , and thus S_{vib}^0 does not have an influence on the calibration procedure. Nevertheless, the calculated S_{vib}^0 can be compared with experimental data to estimate the reliability of the phonons calculations, on which ZPE and $\Delta\Delta H^{0 \rightarrow 298K}$ contributions depend. It is found that the calculated S_{vib}^0 are systematically underestimated with respect to the experimental ones, but all by less than 15%. Besides the fact that these absolute errors are relatively small, we note that they will have an even smaller impact when calculating the $\Delta\Delta H^{0 \rightarrow 298K}$ due to error cancellation. H₂ and H₂O reference gas-phase molecules were treated within the ideal gas framework. The vibrational analysis to estimate their ZPE and $\Delta\Delta H^{0 \rightarrow 298K}$ were carried out with the finite differences method with atomic displacement of 0.02 Å. Experimental data for the solids are taken from references [287, 288], while those for the gas-phase molecules are taken from the NIST-Janaf thermochemical tables.

5.1.2. Calibration of U_{eff}

To calibrate the optimal value of U_{eff} , we referred to the experimental ΔH_{rxn}^0 of the following oxidation reactions:



We considered H₂O and H₂ to avoid including O₂ in the calculations, whose bond energy is overestimated by GGA functionals.[130, 289, 290] We have modelled MnO in the rocksalt structure with antiferromagnetic (AFM) ordering along the (111) planes, spinel Mn₃O₄ (hausmannite) in ferrimagnetic ordering (with Mn²⁺ ions being ferromagnetically and antiferromagnetically aligned among each other and with the Mn³⁺ ions, respectively),[291] α -Mn₂O₃ in ferromagnetic (FM) ordering and β -MnO₂ in AFM ordering. We note that the magnetic ordering had a rather minor impact on the calculated energies considering the accuracy required by the present application. Snapshots of the considered bulk structures are given in Figure 5.1. Importantly, we have included the ZPE and $\Delta\Delta H^{0 \rightarrow 298K}$ both for

the gas-phase molecules and investigated solids, that are often neglected for the latter due to the high computational cost associated to their calculations.

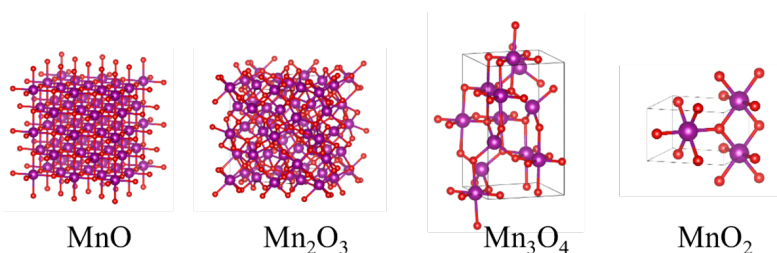


Figure 5.1.: Bulk crystalline structures of manganese oxides.

Figure 5.2 shows the error between predicted and experimental ΔH_{rxn}^0 relative to reactions 5.1, 5.2 and 5.3 with increasing U_{eff} . Noticeably, ΔH_{rxn}^0 increases in a roughly linear fashion by ~ 300 kJ/mol in the investigated range, underscoring that the reducibility of Mn oxides is a strong function of U_{eff} . It is worth noting that the pure DFT approach ($U_{eff} = 0$) tends to over stabilize the oxidized state, likely because the artificial delocalization of the Mn 3d electrons makes them easier to abstract with respect to when they are, correctly, spatially confined. In the calculations of ΔH_{rxn}^0 , the contributions coming from the ZPE and $\Delta \Delta H^{0 \rightarrow 298K}$ reported in Table A.5 amount to -16.0, -18.3 and -17.1 kJ/mol for reactions 5.1, 5.2 and 5.3. On the other hand, those coming exclusively from the solids are smaller and of opposite sign, amounting to 13.9, 11.6 and 12.8 kJ/mol; thus, neglecting them would over stabilize the oxidized state.

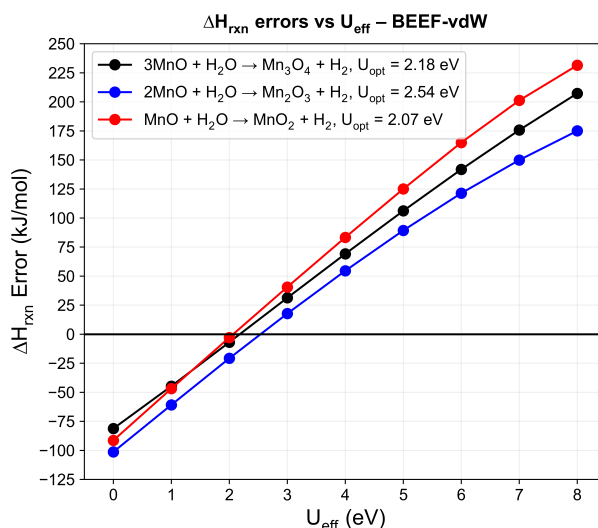


Figure 5.2.: Calibration of U_{eff} against the ΔH_{rxn}^0 of oxidation of MnO to Mn_3O_4 , Mn_2O_3 and MnO_2 .

Importantly, we highlight that the optimal value of the Hubbard correction U_{opt} lies roughly in the range 2 – 2.5 eV for all the reactions investigated, suggesting that U_{opt} is transferable across different oxidation states. This range is close to the one reported by Gautam et al. of 2.5 – 2.9 eV obtained via calculations at the meta-GGA level of theory,[292] but

significantly lower than the one previously reported by Wang et al.[293] and by Franchini et al.[294] of 3.5 – 4.0 eV. One reason for this discrepancy could be that, instead of H₂ and H₂O, they considered O₂ as the gas-phase reference. A further reason is the use of different XC functionals, as both studies have employed PBE+U. We note that albeit a variety of values of U_{eff} for Mn have been reported, usually the choice lies in the 3.5 - 4.5 eV range,[295] might lead to large errors in ΔH_{rxn}^0 in the order of ~ 100 kJ/mol. Even though bandgaps might be well reproduced using this U_{eff} range, such errors in ΔH_{rxn}^0 would yield irreparably flawed results for catalysis applications, underscoring that the semiempirical calibration of U_{eff} should aim at matching the properties of interest for each case study. In the remainder of this thesis, we will use $U_{\text{eff}} = 2.5$ eV for Mn that, based on our results, produces a reliable description of the reactivity of Mn oxides.

5.1.3. Bridging Measured and Calculated Mn Charges

Within the DFT framework, several approaches have been developed to extract atomic charges from the electron density (ρ),[296] among which the Bader analysis is arguably the most widely used.[297–299] In this method, atomic (Bader) volumes are defined by zero-flux surfaces of the electron density, $\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$, which serve as spatial boundaries between atoms. Partial atomic charges are then obtained by integrating the electron density within these volumes.

A conceptually different strategy relies on atomic magmoms to assess the valence of TM ions. These moments are computed by integrating the difference between spin-up and spin-down electron densities over a chosen region of space, which may be defined either as a user-specified sphere centered on the atom or via projections onto atomic orbitals determined by the employed basis set.[151, 300–302] However, neither Bader charges nor atomic magmoms can be directly mapped onto formal oxidation states, which are probed experimentally by techniques such as X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). To overcome this limitation, we have calculated both quantities for the bulk Mn structures shown in Figure 5.1 and the gas-phase molecules listed in Figure 5.3 and outlined their relations to the Mn oxidation states, that can be derived unambiguously from the stoichiometry of the considered structures.

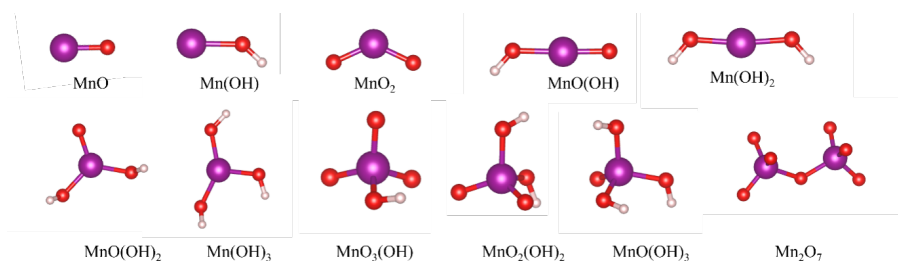


Figure 5.3.: The gas-phase $\text{Mn}_x\text{O}_y\text{H}_z$ molecules considered for mapping the Mn oxidation states .

The resulting Mn oxidation states, magmoms and Bader charges are listed in Table 5.1 and plotted in Figure 5.4 and 5.5. Interestingly, we found that the prediction of the magmom is

Table 5.1.: Oxidation states, magnetic moments and Bader charges of Mn in the investigated bulk oxides and gas-phase $\text{Mn}_x\text{O}_y\text{H}_z$ molecules.

$\text{Mn}_x\text{O}_y\text{H}_z$	Oxidation state	Magmom (μ_B)	Bader charge on Mn (e)
Bulk MnO	+2	4.55	+1.300
Bulk Mn_3O_4	+2/+3	4.54/4.02	+1.446/+1.599
Bulk Mn_2O_3	+3	3.98	+1.656
Bulk MnO_2	+4	2.91	+1.837
$\text{Mn}(\text{OH})$	+1	4.79	+0.676
MnO	+2	4.21	+0.788
$\text{Mn}(\text{OH})_2$	+2	4.47	+1.327
$\text{MnO}(\text{OH})$	+3	4.16	+1.269
$\text{Mn}(\text{OH})_3$	+3	3.80	+1.566
MnO_2	+4	2.64	+1.313
$\text{MnO}(\text{OH})_2$	+4	2.99	+1.586
$\text{MnO}(\text{OH})_3$	+5	2.06	+1.724
$\text{MnO}_2(\text{OH})_2$	+6	1.19	+1.721
Mn_2O_7	+7	0.00	+1.722
$\text{MnO}_3(\text{OH})$	+7	0.00	+1.742

rather consistent with respect to the oxidation states across all the structures investigated. In particular, the magmoms for Mn^{2+} ions are always roughly $4.5 \mu_B$, those for Mn^{3+} are $\sim 4 \mu_B$ and those for Mn^{4+} are $\sim 3 \mu_B$. The magmoms for the higher oxidation states derived from the gas phase molecules of +5, +6 and +7 were roughly 2, 1 and $0 \mu_B$, respectively. Upon loosing the 4s electrons, the electronic configuration of the Mn^{2+} ion is $[\text{Ar}]3d^5$. We notice that the further increase in oxidation states and corresponding decrease of magmom occur in almost a 1:1 fashion, accurately reflecting the progressive depopulation of the 3d orbitals. We note that the magmom vs. oxidation states data match closely the employed quadratic fit (Figure 5.5) that yields $R^2 = 0.985$. Importantly, the same relation holds true both for the bulk and molecular structures, indicating that it can be used successfully to describe systems that are qualitatively very different.

On the other hand, the correlation between the Mn oxidation states and Bader charges is, in comparison, more uncertain. At a given oxidation state, a rather broad range of Bader charges is obtained that extends for 0.67, 0.39 and $0.52 e$ for oxidation state = +2, +3 and +4 respectively. In particular, as shown in Figure 5.5, the data points for bulk and molecular structures seem to lie on two lines with similar slope but offset with respect to each other. Even though, as expected, the Bader charge increases with OS, the linear fit yields rather poor agreement with the data, that is quantified by $R^2 = 0.519$. Additionally, it was found that the Bader charge becomes insensitive on the oxidation state when this becomes larger than +4.

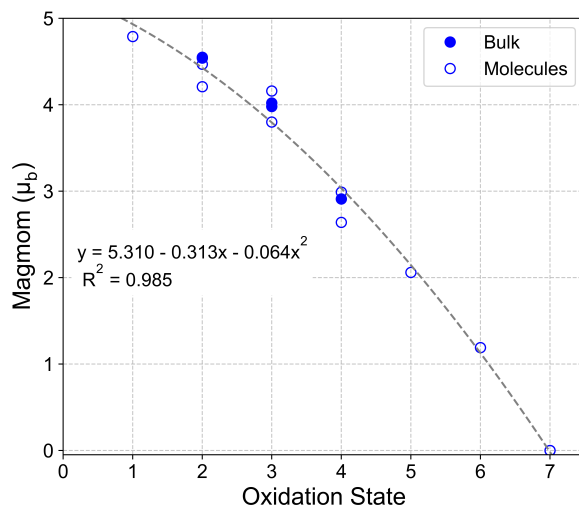


Figure 5.4.: Correlation between Mn oxidation states and magnetic moments in bulk oxides and gas-phase $\text{Mn}_x\text{O}_y\text{H}_z$ molecules.

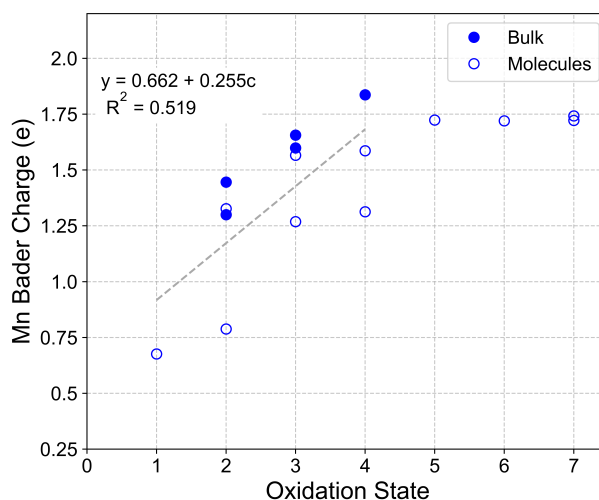


Figure 5.5.: Correlation between Mn oxidation states and Bader charges in bulk oxides and gas-phase $\text{Mn}_x\text{O}_y\text{H}_z$ molecules.

Overall, our results show that the magmom and Bader charges correlations might yield different results when applied to systems where the oxidation state of Mn is not directly derived from the stoichiometry. While it is not possible to state with certainty which correlation would match experimental data more closely, we argue that the Mn magmom is a more reliable descriptor of its oxidation state in light of the better consistency across the investigated dataset.

5.1.4. Conclusions

In this section, we have benchmarked our DFT approach to ensure a correct description of Mn reactivity and oxidation state. While we did not focus on Mn promoted Co catalysts, that are the object of this chapter, the methodology established here will be used in the following sections to obtain reliable results that will shed light on the Mn promotional mechanism. In particular, we will from now on use $U_{\text{eff}} = 2.5$ eV for Mn in our DFT calculations, that will be performed to obtain the DFT labels for the dataset used to train our MLP in section 5.2 and to calculate CO dissociation and O removal reaction paths on a Mn-promoted hcp-Co(0001) surface in section 5.3. Furthermore, we will use the quadratic correlation between Mn oxidation state and magmom derived here to predict the oxidation state of Mn in our models, that will be compared to experimental data available in the literature.

5.2. Structures and Stability of Mn on Co Nanoparticles

5.2.1. Introduction and Methods

Scope. Obtaining realistic models of the active sites is arguably the main bottleneck of DFT calculations in the field of catalysis. The complexity of real catalytic systems, in fact, can hardly be faithfully reproduced within the length scales explorable with DFT, leading computational studies to almost always rely on highly simplified models, often arbitrarily built, that are assumed to represent reality. While this strategy has frequently proven successful in obtaining qualitative insights, it might become too stringent for not well-defined systems for which little *a priori* mechanistic understanding is available. We believe Mn promoted Co catalysts are a perfect example of this case.

To date, different theoretical studies have attempted to clarify the promotional mechanism of Mn.[97, 101, 121–124] While they contributed to advance the current understanding of Mn promotion, the limited scope of the employed models suggests that important aspects might have been left unexplored. In particular, although several models ranging from metallic Mn alloying with Co to atomically dispersed oxidic Mn, cluster and periodic structures adsorbed on Co have previously been proposed, so far only the Co fcc(111) and hcp(0001) terraces have been considered. This greatly limits the transferability of the results to Co NPs, not only because their surfaces are actually characterized by highly diverse atomic configurations, but also because the LCS are the most active sites on the unpromoted catalyst for CO dissociation, that Mn has been shown to enhance. Also the range of compositions of the adsorbed Mn structures has so far been limited, mostly owing to the fact that the models were built to align the stoichiometry to the experimentally reported divalent state of Mn. However, charge transfer from the Co surface might compensate that from Mn to its ligands, causing the Mn oxidation state to deviate from the one expected based on the stoichiometry and greatly enlarging the plausible range of Mn:O:H ratios existing in the promoter structures. Finally, despite significantly affecting

catalyst performance, the effect of Mn loading on its speciation has so far been neglected. One of the reasons for this is that, in periodic models, the number of Mn atoms cannot be linked unambiguously to the experimental Mn loading.

In this section, we combine our DFT based MC approach to model metal NPs, MLPs and GA to obtain holistic models of Mn-decorated Co NPs that overcome the previously discussed limitations. In particular, we identify the low-energy structures of Mn on 6 and 8 nm fcc-Co and 8 nm hcp-Co NPs via an fine-tuned MLP-powered GA. For each NP model, we investigate five different Mn stoichiometries and loadings and outline important energy trends and structural features. The resulting phase diagrams indicate that, while after activation the Mn stoichiometry is MnO – MnO_{1.5}, the lower temperature and high p_{H₂O} during FT cause a transition to hydroxylated structures. Mn was found to bind strongly to the Co NPs, although increasing promoter loading led to a substantial weakening of the metal–promoter interactions. Structural analysis of the low-energy configurations generated during the GA searches revealed that Mn preferentially forms monolayer-like, largely amorphous patches on the Co surface, whose local structural features largely determine their final configurations. The pronounced affinity of Mn for the Co LCS provided the basis for formulating hypotheses regarding the underlying promotional mechanism. Finally, we predicted the oxidation state of Mn in our models, that was consistently found to be close to +2, irrespective of NP model, Mn phase, or promoter loading. This behavior was attributed to a charge-compensation mechanism involving the Co surface, which stabilizes Mn in the particularly favorable +2 electronic configuration regardless of the nominal stoichiometry of the promoter phase.

The results presented in this section are included in the following publication:

Sireci, E.; Hoffman, J.-A.; Gambu, T.; Sharapa, D. I.; Studt, F.; van Steen, E. Elucidating Mn Promoter Structure and Stability on Co Nanoparticles through Machine Learning Potential-Powered Genetic Algorithm. *ACS Catalysis* **2026**.

Methods. DFT calculations were carried out with the same settings as in the previous chapters, with $U_{\text{eff}} = 2.5$ eV for Mn according to the calibration carried out in section 5.1. Thermal corrections were included for the gas-phase reference molecules (H₂ and H₂O) within the ideal-gas approximation and for the calculated GM within the harmonic approximation. For the latter, the $\text{ZPE} + \Delta\Delta H^{0 \rightarrow 500\text{K}} - T\Delta S$ contributions for adsorbed O and OH groups were calculated within the harmonic approximation and as a function of temperature from two hypothetical MnO₂ and MnO₂H clusters adsorbed on fcc-Co(111), whose vibrations were calculated with DFT. The energies of the different Mn_xO_yH_z@Co phases reported throughout this work are predicted from the GM structures identified in each run upon removal of the He atoms. During the GA runs, all candidates were relaxed until the maximum residual force was below 0.075 eV/Å. To eliminate unphysical geometries produced during crossover, all candidates underwent an initial pre-relaxation of 20–40 ionic steps (depending on Mn loading) using the original CHGNet potential. This step was necessary to ensure robustness, as the fine-tuned potential occasionally failed when applied directly to highly distorted structures. In the rare cases where failures persisted after pre-relaxation, the corresponding offspring was discarded and replaced by a newly generated candidate.

5.2.2. MLP Fine-Tuning

The size of the systems we aim to investigate as well as the large number of candidates that are screened throughout the GA runs impose the use of a cheap internal calculator. Following the latest developments in the field, MLPs have become an attractive alternative to quantum chemical methods, as they are now capable to achieve near DFT-accuracy at a fraction of the costs. Following in the footsteps of recent works,[157, 303, 304] here we employ an MLP as internal calculator in the GA runs, more specifically the universal machine-learning potential (uMLP) CHGNet.[151] Being trained over very large datasets that cover most of the periodic table, uMLPs offer the advantage of being extremely robust while requiring only relatively small refinement to reach very high accuracy for a given application. CHGNet is particularly advantageous for our case study since it can also be trained on and predict atomic magmoms, and therefore can be used to derive Mn oxidation states on Co NPs via the correlation derived in Section 5.1.

In order to increase its accuracy, we fine-tuned the original CHGNet model on a dataset of $\text{Mn}_x\text{O}_y\text{H}_z$ structures on periodic fcc-Co surfaces, that was constructed through a series of GA runs using the original potential as internal energy calculator. Each GA run yielded 25 structurally diverse configurations, of which 5 were stored for the test set. In total, 100 GA runs were performed, yielding 2000 structures for the training set and 500 structures for the test set. The dataset spans a broad chemical and structural space, including:

- five $\text{Mn}_x\text{O}_y\text{H}_z$ stoichiometries, namely MnO, $\text{MnO}_{1.5}$, MnO_2 , $\text{MnO}_2\text{H}_{0.5}$ and MnO_2H ;
- four Mn loadings, ranging from two to five Mn atoms;
- five periodic fcc-Co surfaces, namely (111), (100), (110), (311), and (321).

In addition, the training set was augmented with geometry optimization trajectories of previously computed Mn clusters on Co surfaces, clean Co slabs, bulk fcc-Co, and bulk Mn oxide phases. The final training dataset comprised approximately 2500 structures, five of which, chosen as examples, are presented in Figure 5.6.

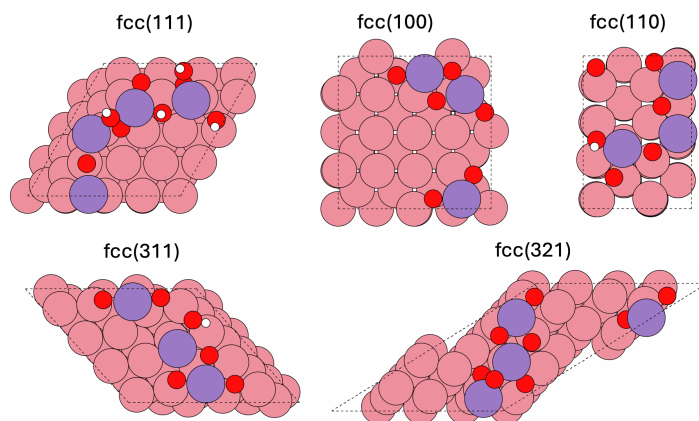


Figure 5.6.: Snapshots of five sample $\text{Mn}_x\text{O}_y\text{H}_z$ structures employed in the training set.

To further assess the transferability of the model, 18 additional GA runs were carried out for three stoichiometries (MnO , MnO_2 , and MnO_2H), two Mn loadings (two and four atoms), and three hcp-Co surfaces ((10-10), (10-11), and (10-12)). These runs yielded additional 360 structures, which were included exclusively in the test set. The DFT labels used throughout training and validation were obtained via DFT SP calculations on the dataset structures with the calculation settings specified in the methods section. The dataset, excluding the 500 $\text{Mn}_x\text{O}_y\text{H}_z@\text{fcc-Co}$ and 360 $\text{Mn}_x\text{O}_y\text{H}_z@\text{hcp-Co}$ test structures, was randomly split into training (90%), validation (5%), and test (5%) sets with a batch size of 8. Transfer learning was employed by freezing the embedding layers and the majority of the graph convolution layers, while optimizing the remaining layers. Training was performed for 2400 epochs using the Adam optimizer with a learning rate of $5\text{E-}3$, a cosine learning rate scheduler, and a mean squared error loss function applied to energies, forces, and magnetic moments. The resulting fine-tuned potential exhibits mean absolute errors (MAEs) of 1 meV/atom for energies, 20 meV/Å for forces, and 8 $\text{m}\mu_B/\text{atoms}$ for magnetic moments, which is within the accuracy of application-specific MLPs.[150, 305–311] Additionally, we evaluated the accuracy of the MLP in terms of formation energies of Mn clusters according to the following equations:

$$x\text{MnO}_{\text{bulk}} + y\text{H}_2\text{O}_{(g)} + \text{Co}_{\text{slab}} \rightarrow \text{Mn}_x\text{O}_{x+y}\text{H}_z@\text{Co}_{\text{slab}} + \left(y - \frac{1}{2}z\right)\text{H}_2 \quad (5.4)$$

$$\Delta E^f = \left(E_{\text{Mn}_x\text{O}_y\text{H}_z@\text{Co}_{\text{slab}}} + \left(y - \frac{1}{2}z\right)E_{\text{H}_2} - E_{\text{Co}_{\text{slab}}} - yE_{\text{H}_2\text{O}} - xE_{\text{MnO}_{\text{bulk}}}\right)/x \quad (5.5)$$

The test set for the formation energies validation comprised the previously excluded 500 $\text{Mn}_x\text{O}_y\text{H}_z@\text{fcc-Co}$ and 360 $\text{Mn}_x\text{O}_y\text{H}_z@\text{hcp-Co}$ test structures. As shown in Figure 5.7, the accuracy of the MLP dramatically improved upon fine tuning, as the MAE of ΔE^f decreased from 271 to 25 meV/Mn atom. Furthermore, the training is well converged with respect to training set size, as the accuracy of the MLP does not change from the training to the test set.

In Figure A.9, we also present the parity plot comparing the formation energies of $\text{Mn}_x\text{O}_y\text{H}_z$ clusters on hcp-Co surfaces as computed using DFT and the fine-tuned CHGNet potential. As anticipated, the performance deteriorates relative to fcc-based systems, yielding a mean absolute error (MAE) of 74 meV, since hcp-Co structures were not included in the training dataset. Nevertheless, this error remains substantially lower than that obtained with the zero-shot potential. Moreover, the deviation is largely dominated by a systematic overstabilization of the structures predicted by the MLP with respect to DFT, suggesting that the relative energies are still captured accurately.

5.2.3. GA Runs

The NP models employed for the GA runs were 6 and 8 nm fcc-Co and 8 nm hcp-Co NPs. Among the 40 lowest-energy structures obtained from each MC run, we selected those with the energy closest to the ensemble average as they are the most representative

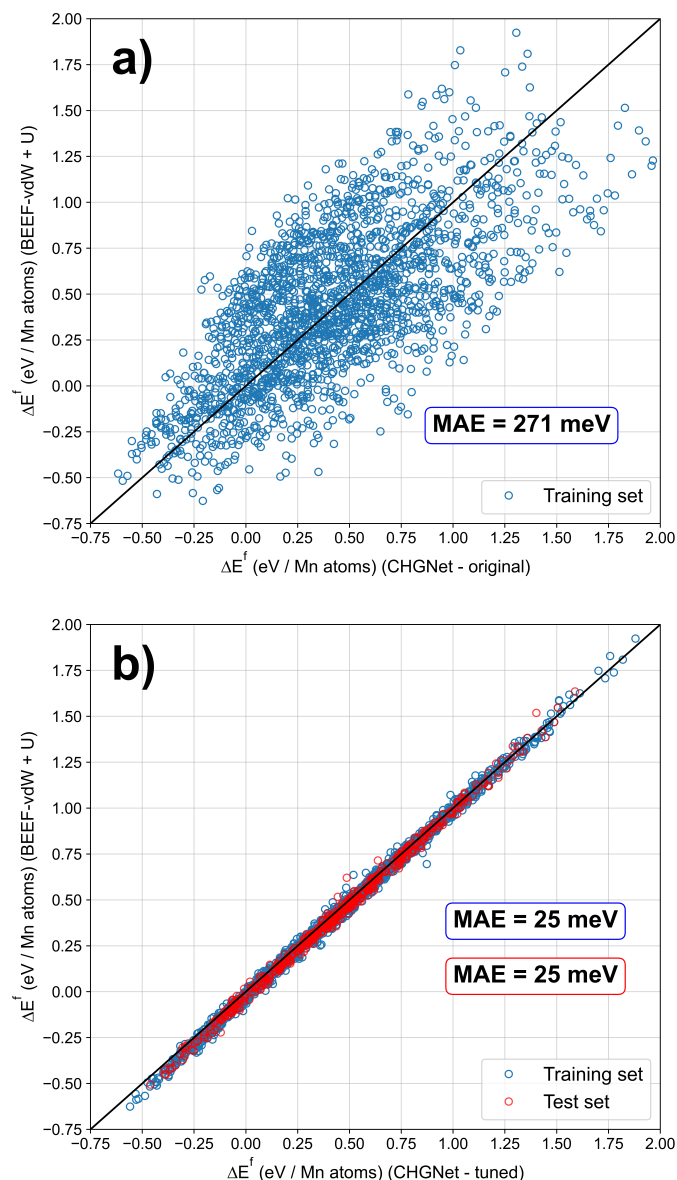


Figure 5.7.: Parity plots of $\text{Mn}_x\text{O}_y\text{H}_z@\text{fcc-Co}$ clusters formation energies as defined in Equation 5.5 calculated with DFT and a) the zero-shot and b) the fine-tuned CHGNet MLP. The data points in a) were all shifted by a constant energy that minimized the MAE, so that systematic errors coming from inaccurate zero-shot CHGNet calculation of the reference structures are not considered.

of the entire ensemble. We reduced computational cost by cutting the NPs along their symmetry planes, yielding models that are roughly 1/4 and 1/8 of the original 6 and 8 nm particles, respectively. Furthermore, we removed a portion of the inner Co atoms so that the resulting NP shell is at all points at least 4 Co layers thick, ultimately resulting in NP slabs of roughly 2000 Co atoms. To prevent Mn clusters from migrating over the artificial edges of the models, we covered them with He atoms that provided steric hindrance. All the He atoms as well as the Co atoms at the cut locations and in the two innermost layers

of the employed NP shells were frozen during optimization, while the two top layers of Co atoms were allowed to relax. The resulting slab models are shown in Figure 5.8.

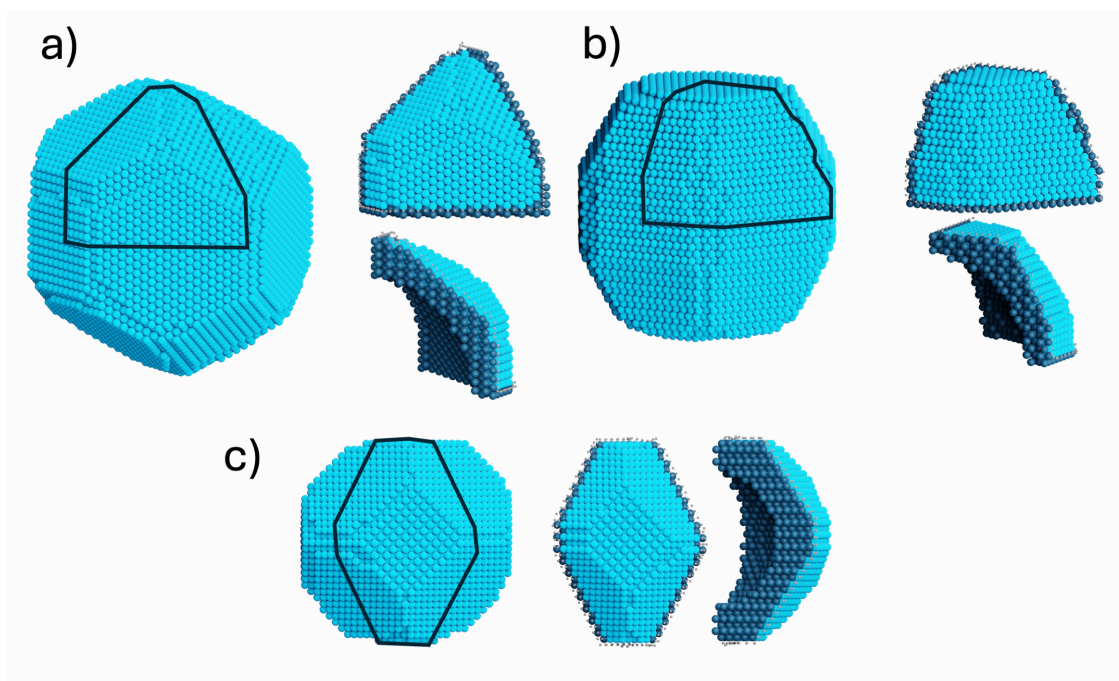


Figure 5.8.: NPs (left) and frontal and side views (right) of corresponding slab models employed in the GA runs for 8 nm a) fcc-Co, b) hcp-Co and c) 6 nm fcc-Co. Frozen Co and He atoms are depicted in dark blue and grey, respectively.

We employed a modified, pool-based implementation of the genetic GA available in the Atomic Simulation Environment (ASE),^[152, 153] using a population size of 30 candidates. The initial population was generated by randomly placing formula units of the selected $\text{Mn}_x\text{O}_y\text{H}_z$ stoichiometry on the Co surface, with the constraint that Mn atoms were located within 4 Å of the nearest Co atom while avoiding unphysically short interatomic distances. Offspring generation was performed via a cut-and-splice crossover operation, with parent selection based on a fitness criterion that accounts for both energetic stability and the frequency with which a candidate had already been selected for reproduction. Following crossover, O atoms not bound to Mn were randomly positioned near Mn atoms, with a higher probability of attachment to undercoordinated Mn sites. Likewise, H atoms not bound to O were placed adjacent to randomly selected dehydroxylated O atoms. This strategy prevents the formation of structures in which O and H bind independently to the Co surface, which are outside the scope of this study, while simultaneously allowing for O and H rearrangements that enhance population diversity. Prior to structural relaxation, offspring candidates were subjected to mutation with a probability of 0.35. Two mutation operators were employed: a standard rattle mutation and a custom mutation that relocates $\text{Mn}_x\text{O}_y\text{H}_z$ units to unoccupied, low-coordinated ($\text{CN} \leq 7$) Co sites on the slab. We note that this mutation does not introduce a bias in the sampling of the PES, since the mutant candidates would not be included in the population pool if they were not, indeed, particularly stable. The rattle and custom mutations were applied with a probability ratio of

1:4, respectively. After relaxation, an offspring was admitted to the population if it was both structurally distinct from existing candidates and more stable than the least stable member of the pool, which it subsequently replaced. Two structures were considered identical if their relative cumulated distance difference and maximum pairwise distance difference were below 0.25 and 3.0 Å, respectively, and if their energies differed by less than 0.1 eV. The rationale for these similarity criteria follows the methodology established by Vilhelmsen and Hammer.[152, 153] An energy-based screening was applied during optimization, whereby structures that remained significantly higher in energy than the current global minimum after 20-40, depending on Mn loading, ionic steps were discarded. Convergence of the GA search was achieved when no structure more stable than the previously identified GM by more than 5 meV per Mn atom was found among the last 600 evaluated candidates. We investigated five Mn stoichiometries, namely MnO, MnO_{1.5}, MnO₂, MnO₂H_{0.5}, and MnO₂H, across five different Mn loadings corresponding to Mn:Co molar ratios of 0.01, 0.02, 0.03, 0.04, and 0.05. These ratios translate to 25, 50, 75, 100, and 125 Mn atoms for the 6 nm fcc-Co slab, and 30, 60, 90, 120, and 150 Mn atoms for the 8 nm fcc- and hcp-Co slabs. The Mn atom counts were derived from the total number of Co atoms in the corresponding uncarved NPs (10152 and 24064 for the 6 and 8 nm models, respectively) and subsequently scaled by factors of 4 and 8 for the 6 and 8 nm slab representations.

5.2.4. Stability of Mn on Co Nanoparticles

We have investigated the most favorable Mn phase on Co NPs under changing thermodynamic conditions by building phase diagrams (Figure 5.9) considering a typical FT feed of 20 bar and H₂:CO = 2:1 at varying X_{CO} levels, from which the p_{H₂O}/p_{H₂} ratio is determined. Phase diagrams at reduction conditions (feed of 1 bar, pure H₂) are shown in Figure A.10. We calculated the Gibbs free energies of formation of the GM (ΔG_{GM}^f) (without He atoms) identified in each run according to the following equation:

$$\Delta G_{GM}^f = \Delta G_{GM}^{Mn_xO_yH_z} + \left(y - \frac{1}{2}z\right) \mu_{H_2} - E_{Co_{slab}} - xE_{MnO_{bulk}} - y\mu_{H_2O} \quad (5.6)$$

Where $\Delta G_{GM}^{Mn_xO_yH_z}$ is the Gibbs free energy of the GM (potential energy + thermal corrections) and $E_{Co_{slab}}$ is the potential energy of the Co NP slab. For each Co NP model, five different Mn loadings ranging from 0.01 to 0.05 were investigated. We note that albeit nominal experimental Mn loadings are often larger, they correspond to a lower loading on the Co NPs due to the fact that, in real catalysts, a portion of the promoter is deposited on the support.

The phase diagrams reveal that, except for Mn:Co = 0.01 on the 8 nm hcp-Co NP, the MnO₂H_{0.5} and MnO₂H phases are always the most stable ones under FT conditions, indicating that the Mn centers are functionalized with hydroxyl groups that may play a role in the reaction network. Nonetheless, the Mn structures are considerably affected

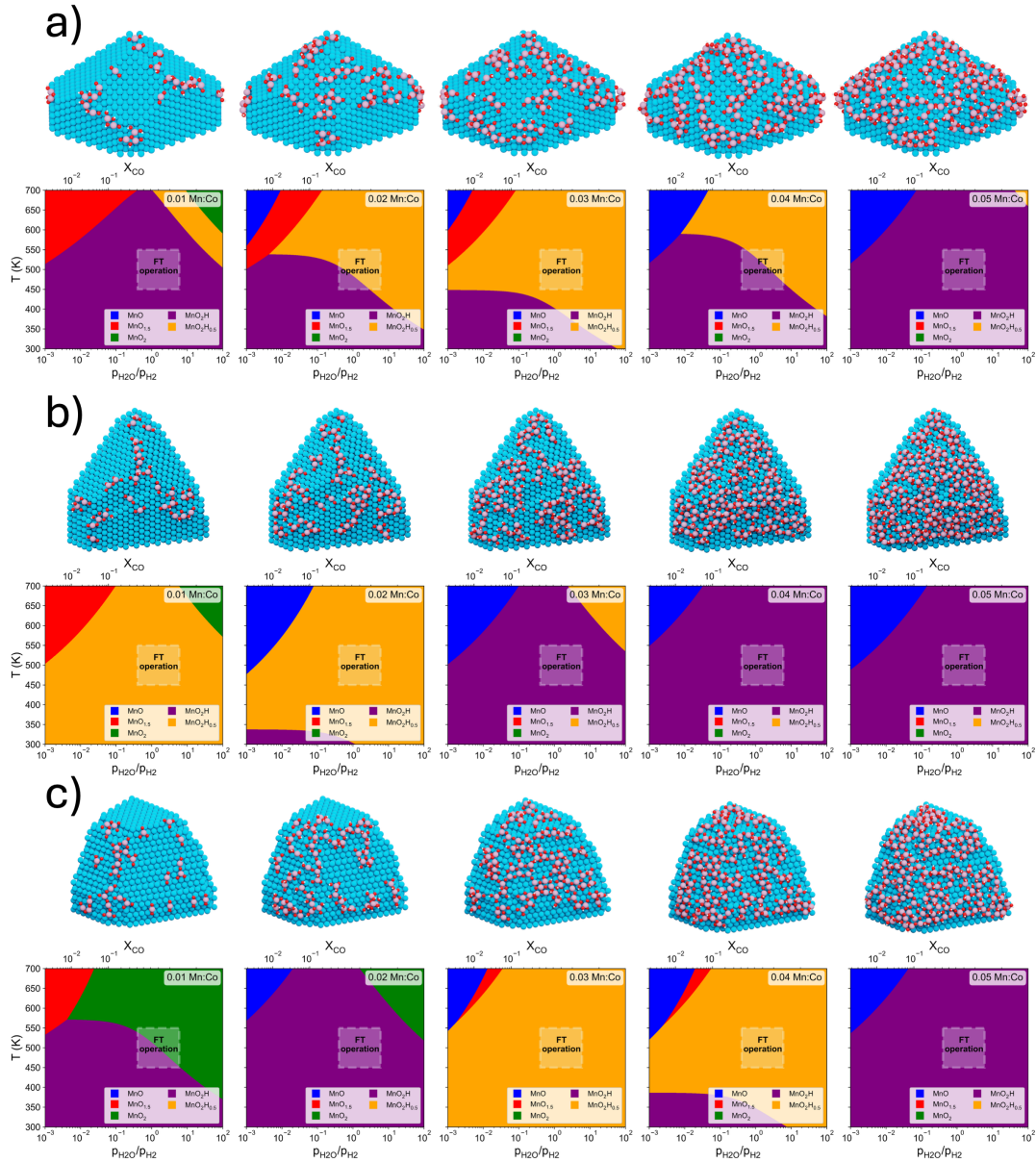


Figure 5.9.: Phase diagrams of Mn structures with loadings ranging from 0.01 to 0.05 Mn:Co on a) 6 nm fcc-Co NP slab, b) 8 nm fcc-Co NP slab and c) 8 nm hcp-Co slab. Snapshots of the most stable phases under FT conditions are included above the respective phase diagrams.

by changing thermodynamic conditions between FT and reduction, where the higher temperatures hinder H_2 and H_2O adsorption and thus favor the MnO and $\text{MnO}_{1.5}$ phases.

Additionally, we observe that the effect of increasing Mn loading is to favor the formally more reduced phases, which can be seen by the disappearance of the MnO_2 phase and by the gradual substitution of the $\text{MnO}_{1.5}$ and $\text{MnO}_2\text{H}_{0.5}$ phases by the MnO and MnO_2H ones, respectively. This occurs because increasing loading drives the Mn structures closer

together, causing electrostatic repulsion between the negatively charged O and OH ligands. Additionally, while OH ligands are rather geometrically flexible, O adsorbates are more rigid as they tend to be anchored to the Co surface, and therefore hinder the formation of compact structures. This trend is reproduced across all the investigated NP models, even though the phase boundaries at a given loading are often considerably shifted. In particular, the boundary between the two hydroxylated phases appears rather labile across NP models, which is due, as we will show shortly, to the fact that these structures are often very close in energy and thus the boundary between them can change significantly within the uncertainty window of the calculations. The snapshots of the GMs presented in Figure 5.9 indicated a preference for the formation of monolayer-like, mostly amorphous, Mn structures, that are shaped around the NPs surface conformations. Nonetheless, the structures appear vastly different across the different loadings, as for $\text{Mn:Co} \leq 0.02$ Mn forms highly dispersed mononuclear or linear structures largely localized on the NPs LCS, while for the larger loadings Mn is increasingly found in 2D patches that densely populate the whole NPs surfaces.

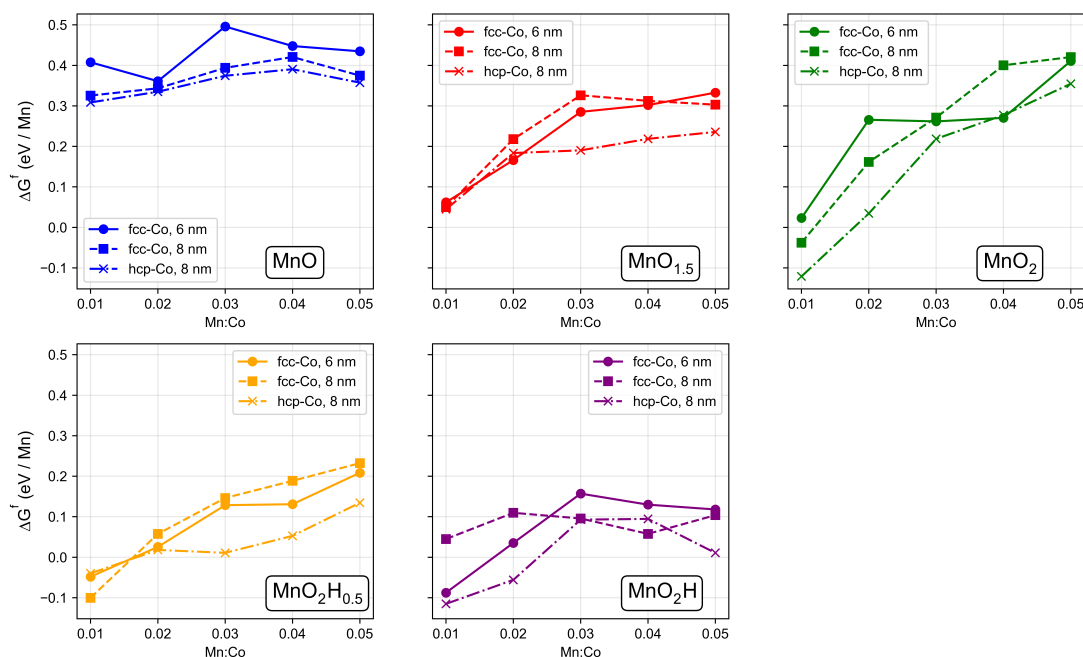


Figure 5.10.: Formation Gibbs free energies (ΔG^f) calculated according to Equation 5.6 at $T = 500$ K and $X_{\text{CO}} = 75\%$ of the investigated $\text{Mn}_x\text{O}_y\text{H}_z$ phases on the three Co NP slab models with increasing loadings.

In Figure 5.10, we compare the stability of the different Mn phases at FT conditions ($T = 500$ K, $X_{\text{CO}} = 75\%$) across different loadings and NP models. Strikingly, for all phases except MnO where this effect is less pronounced, increasing loading significantly destabilizes the promoter structures. In particular, the ΔG^f differences between the highest and lowest loadings for the MnO_2 , $\text{MnO}_2\text{H}_{0.5}$, $\text{MnO}_{1.5}$ and MnO_2H are as high as 0.45, 0.32, 0.25 and 0.22 eV/Mn atom, respectively, even though these values change across NP models. This is ascribed to two factors. On the one hand, as mentioned above, increasing Mn coverage causes electrostatic repulsion between the Mn units and induces a distortion of

the structures so that more Mn can be accommodated on the NP surface. This hypothesis is corroborated by the fact that the destabilization is larger the more formally oxidized the Mn phase. On the other, as we will show in the next subsection, Mn preferentially binds to the Co LCS, that become almost fully covered early on. Thus, with further Mn addition, only the Co terraces are left available, where Mn adsorbs weakly and is therefore less stable. This implies that not all the Mn species are equivalent, as those that bind to the LCS are strongly anchored and thereby highly persistent, while those deposited on the terraces are likely more prone to removal and might migrate to the support during activation or, more likely, during FT, as CO molecules are expected to displace the weakly binding species. Under reaction conditions, the portion of promoter that detaches from the Co NPs likely depends on the specific Mn-support interactions, implying that the same experimental Mn loading results in different Co coverages depending on the support. We note that the reported optimal Mn loadings are typically smaller on SiO₂-supported[99, 101] Co catalysts with respect to Al₂O₃[97] and TiO₂,[312], indicating that the Mn-support interactions are more favorable on the latter oxides.

A comparison ΔG^f across the different NP models highlights that both the crystal lattice and particle size do not significantly affect the stability of Mn. We note, however, that the Mn structures are generally more stable on the 8 nm hcp-Co than on the fcc-Co NP, with average (over the different Mn loadings) ΔG^f of -0.02, -0.07, -0.09, -0.07 and -0.08 eV/Mn atom for the MnO, MnO_{1.5}, MnO₂, MnO₂H_{0.5} and MnO₂H phases, respectively. Nonetheless, these differences are rather small and it is therefore unlikely that Mn promotion significantly affects the competition between the two crystal phases. We thus cautiously rule out the possibility that the main promotional effect of Mn is to increase the proportion of hcp-Co in the catalyst, that has been shown to be more active and more selective to C₅₊ products than its fcc counterpart.[57, 58, 63]

We additionally observe that the most stable Mn structures, i.e. MnO₂H_{0.5} and MnO₂H for Mn:Co $\leq$ 0.02, are either more or roughly as stable as MnO bulk, that was used as reference in Equation 5.6. This underscores the high stability of these Mn structures adsorbed on Co and aligns with the intimate contact between the metal and the promoter widely reported experimentally. Furthermore, in light of their strong anchoring to the Co surface, this indicates that at least a portion of the Mn species likely maintain stability and promotional activity over long reaction periods.

Finally, Figure 5.10 shows that the different Mn phases and especially the two hydroxylated ones, that are also the most stable, are generally very close in energy, with the differences at a given loading often not exceeding 0.1 eV/Mn atom. This suggests that the Mn structures readily rearrange under FT conditions, and we argue that this flexibility might be at the heart of their promotional activity. The small energy difference between structures with different degrees of hydroxylation, in fact, indicates that the O and OH ligands can easily accept or donate H and could thus function as proton shuttling centers, enhancing the hydrogenation reactions in the FT network. These are CO hydrogenation to HCO and COH species– precursors of CO dissociation according to the H-assisted mechanism – as well as hydrogenation of the growing hydrocarbon chains and O removal. We note that it was previously predicted that the latter step would be facilitated by Mn decoration,

which is also in agreement with the reported excellent resistance against oxidation of the Mn-promoted Co catalysts under operation even at high X_{CO} . [58] Moreover, the OH groups could themselves undergo hydrogenation and desorb, creating vacancies that could serve as particularly reactive sites for CO dissociation according to a reverse Mars-van Krevelen mechanism, [313–316] which has been previously proposed for Mn-promoted Co FT catalysts and predicted to greatly enhance CO dissociation rates. [101]

5.2.5. Promoter Structural Characterization

Herein, we present a structural analysis of the GA runs trajectories, that contained only the candidates whose energies were lower than $E_{\text{GM}} - n_{\text{Mn}} \cdot 0.02$ eV, where E_{GM} is the energy of the GM and n_{Mn} is the number of Mn atoms. Reported error bars are the MADs with respect to the values averaged over the considered candidates.

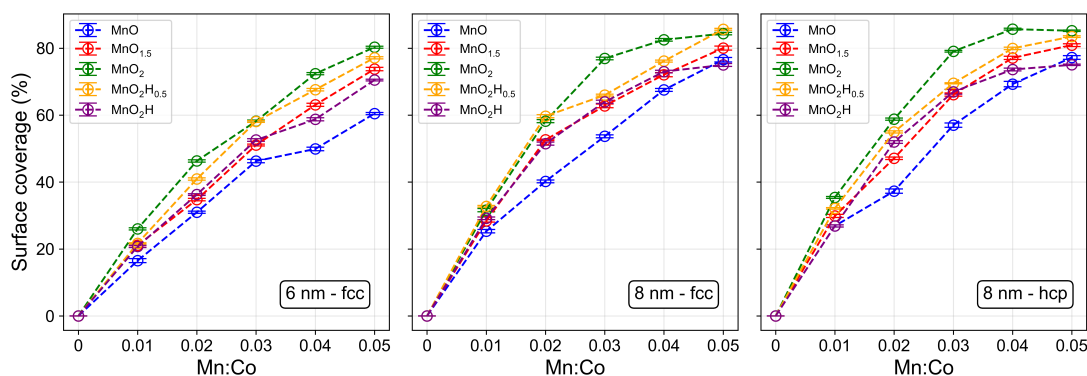


Figure 5.11.: Surface coverage of the Co NPs slabs with increasing Mn loading. Co atoms were considered covered when the Co–O and Co–Mn distances were lower 2.15 Å and 3.0 Å, respectively.

The Co NPs surface coverage is presented in Figure 5.11. At a given Mn loading, the 6 nm fcc-Co NP is always more densely covered than the 8 nm fcc and hcp-Co counterparts, due to the fact that the former exposes a larger surface area per Co atom in light of its reduced size. We note that while on the 6 nm NP the coverage increases mostly linearly with Mn loading, on both 8 nm models the curves approach a plateau for $\text{Mn:Co} \geq 0.04$ due to the formation of sporadic non-monolayer Mn structures. Surface coverage changes notably across the different Mn phases, with differences as high as 20% between the MnO₂ and MnO phases. Coverage increases with O:Mn ratio, due to the fact that O ligands tend to bind simultaneously to Mn and the Co surface, whilst it decreases with O:H ratio, as hydroxyl groups are more flexible and are often detached from the Co surface. We note that Johnson et al. [98] reported significantly lower Co coverage as measured via H₂ chemisorption of 10 and 40% for Mn:Co ratios of 0.01 and 0.05, respectively. We argue that one of the reasons for this discrepancy is that the promoter itself might have adsorbed H₂ during the experiments, leading to an overestimation of the available Co surface area. In fact, while measuring the adsorption isotherms, they exposed the reduced catalysts to an H₂ atmosphere at 373 K. Hence, according to our calculations, at the start of the

experiment Mn was in the $\text{MnO-MnO}_{1.5}$ state and likely adsorbed H_2 throughout the measurement as the lower temperature triggered a transition to the hydroxylated phases. Another important factor to consider is that, since a portion of Mn always covers the support and not the Co NPs, a given nominal experimental loading always corresponds to a lower one in our models.

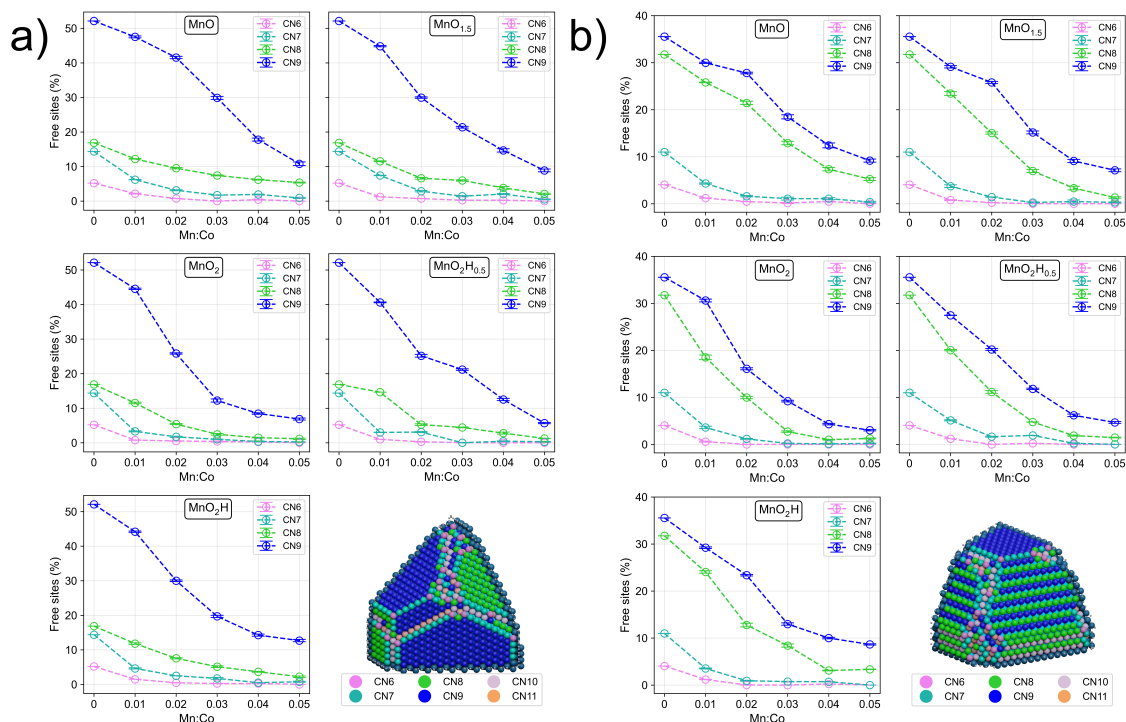


Figure 5.12.: Percentage of free Co sites with different CNs with increasing Mn:Co ratios for all the investigated Mn phases on the 8 nm a) fcc-Co and b) hcp-Co NPs.

As we have shown in Chapter 3, not all the sites on the Co NPs are equivalent and the preferential location of Mn on the metal surface might have significant implications for catalytic performances. Thus, we kept track of the percentages of free Co sites with different CN for the investigated Mn phases and loadings, that are presented in Figure 5.12 for the 8 nm fcc and hcp-Co NPs and for the 6 nm fcc-Co NP in Figure A.11. As highlighted in the snapshots of the Co slabs where the atoms are colored based on their CN, the Co sites with CN = 6 are found at the corners and kinks, those with CN = 7 at the steps and edges and those with CN = 8 are predominantly found on the (100) terrace on the fcc model, while on the hcp NP they are located on the (10-11) and (10-10) surfaces. Additionally, Co atoms with CN = 9 are found on the fcc(111), hcp(0001) and hcp(10-11) terraces. Co atoms with CN = 10 and 11 are found at the base of the B5-A and B5-B step sites and hardly bind to any adsorbate since they are highly shielded. As they diminish only slightly with Mn loading, these sites are not displayed in the plots of Figure 5.12.

The percentages of all available Co sites decrease with Mn loading, but, importantly, this occurs to a larger extent for the low-coordinated atoms (i.e., CN = 6 and 7) that already from Mn:Co = 0.02 are almost fully occupied. On the other hand, the terrace Co

atoms (CN = 8 and 9) initially decrease mildly, while become densely covered only when the LCS are largely unavailable. This indicates that Mn preferentially binds to the LCS on the Co surface, which was already visible from the snapshots of the GMs shown in Figure 5.9. As we mentioned earlier, this is one of the main factors that causes increasing loading to destabilize the Mn structures, as the low-coordinated Co sites where Mn binds strongly are largely covered early on, and further Mn additions lead to formation of less stable structures adsorbed on the terraces. The same behavior is observed across all Mn phases and NP models, underscoring the general character of this conclusion. Notably, however, on the hcp model Co atoms with CN = 8 are more abundant than on the fcc counterparts, due to the fact that they are largely present, together with CN = 9 atoms, on the predominant (10-11) facets. Interestingly, on the hcp model Mn binds preferentially to the CN = 8 atoms than to the CN = 9 ones. This is highlighted by the fact that, while the two sites are present in similar concentrations in the absence of Mn, as the promoter loading increases the available CN = 8 Co decrease significantly more, made exception for the MnO phase. We ascribe this to the particularly favorable conformation for Mn adsorption on the hcp(10-10) facets, where CN = 8 atoms are predominant.

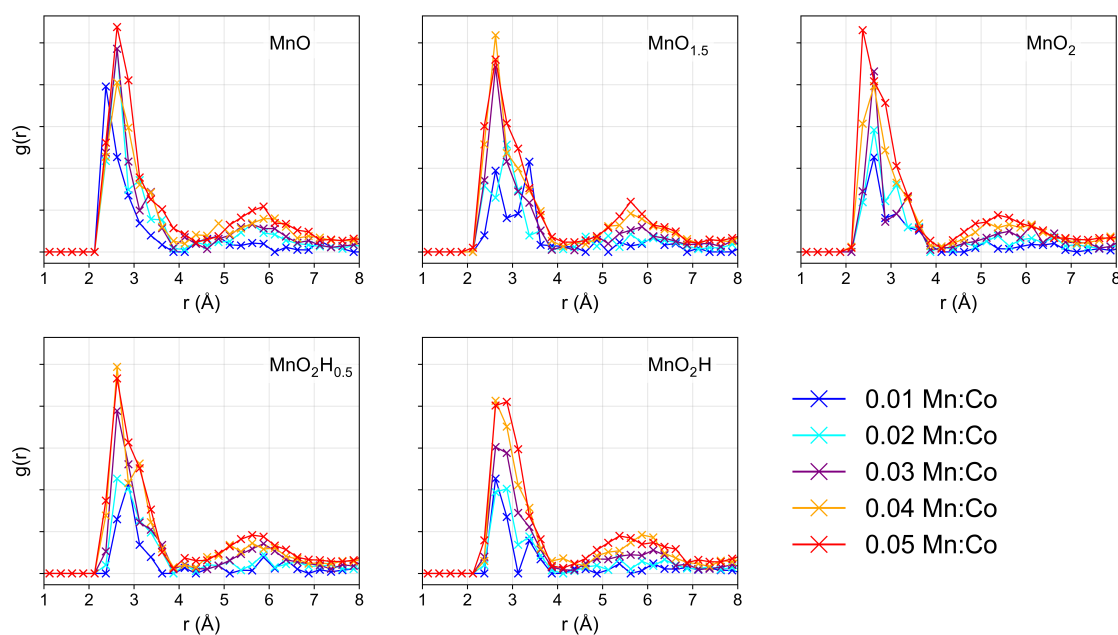


Figure 5.13.: Mn-Mn radial distribution functions ($g(r)$) for the different Mn phases on the 8 nm fcc-Co slab with increasing loading.

The Mn-Mn radial distribution functions ($g(r)$) as a function of Mn loading and phase (shown in Figure 5.13 for the 8 nm fcc-Co NP, Figures A.12,A.13 for the other NP models) is characterized by two main peaks, one for the first Mn-Mn coordination shell located roughly between 2.2 and 4 Å, and another for the second shell located between 4.5 and 6.5 Å. As expected, with increasing loading both peaks increase sharply, indicating agglomeration of the different Mn structures. The fact that the first peak is, in all cases, significantly more intense than the second further indicates that Mn tends to form small islands that lack long-range order. This highlights that the formation of Mn structures is mainly driven by

Table 5.2.: The ratios between the areas underneath the first and second peaks of the Mn-Mn radial distribution functions as a function of Mn phase and loading on the 8 nm fcc-Co model.

MnO_xH_y	Mn:Co				
	0.01	0.02	0.03	0.04	0.05
MnO	4.9	3.3	2.8	2.1	2.2
MnO _{1.5}	3.5	2.9	3.3	2.6	2.4
MnO ₂	5.2	3.5	2.7	2.6	2.7
MnO ₂ H _{0.5}	3.2	3.3	2.5	2.6	2.4
MnO ₂ H	4.6	3.2	2.5	2.1	2.2

the Co NPs surface conformation, as binding to the most favorable sites yields a larger energy gain than the formation of bigger, crystalline Mn conglomerates. Nonetheless, the ratios between the areas under the two peaks shown in Table 5.2 consistently decrease with Mn loading, indicating that the formation of a ordered crystalline Mn overlayer might take place as more and more promoted is deposited on the Co NPs.

No significant differences are observed in the Mn-Mn $g(r)$ across the different Mn phases, indicating that they all adopt qualitatively similar structural motifs. When comparing the various slab models, the increase in the intensity of the first and second coordination peaks with Mn loading is less pronounced for the 6 nm fcc-Co NP than for the 8 nm fcc- and hcp-Co ones. This behavior can be attributed to the larger surface area relative to the number of Co atoms in the smaller NP, which results in a lower effective Mn surface coverage for the same nominal loading.

5.2.6. Derivation of Mn Formal Oxidation State

In Figure 5.14, we present the calculated Mn oxidation states as a function of Mn phase and loading on the three investigated NP models. These were obtained from the prediction of the magmoms of the Mn atoms in the identified GM structures via the fine-tuned CHGNet potential, that were then translated to the oxidation states based on the correlation depicted in Figure 5.4.

Strikingly, we observe that the predicted Mn oxidation state is independent on Mn loading, stoichiometry and NP models and is always roughly +2, even though the formal oxidation states of the Mn phases range between +2 and +4. We note that the observed differences in the range of 0.1-0.2 μ_B are within the uncertainty of the employed correlation and thus likely do not arise from any underlying physical effect. The discrepancy between the nominal and formal oxidation states can be explained, as mentioned earlier, based on a charge compensation mechanism where the Co surface donates electrons to the Mn clusters, thus compensating the charge transfer to the O and OH ligands from the Mn cations, that therefore maintain the divalent state. Interestingly, the resulting oxidation of the Co surface might alter its reactivity. This phenomenon has a strong self-regulating character, demonstrated by the fact that it is mostly absent for the MnO phase, for which the nominal and formal oxidation states largely align, and grows stronger the more oxidized

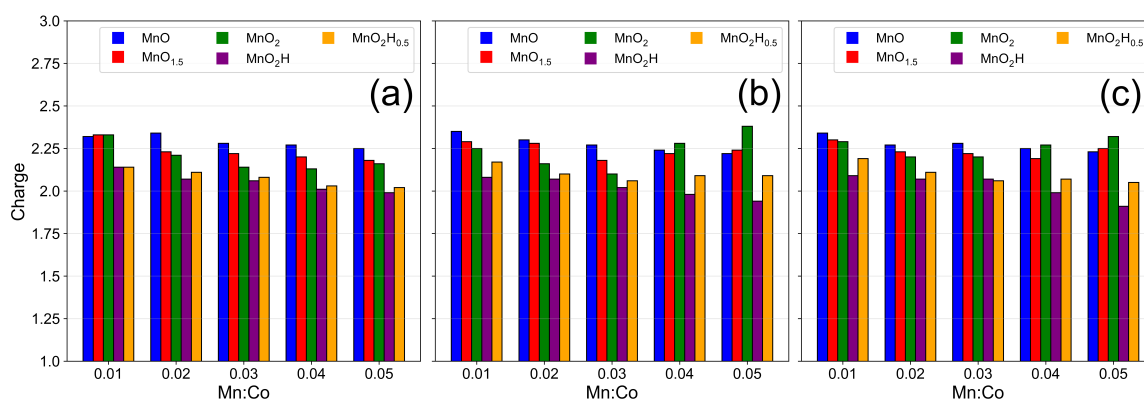


Figure 5.14.: Predicted Mn average Mn oxidation states as a function of Mn phase and loading on a) the 6 nm fcc-Co NP, b) the 8 nm fcc-Co NP and c) the 8 nm hcp-Co NP.

the system becomes. We argue that the marked tendency of Mn ions to preserve the 2+ oxidation state arise from the exceptional stability of the corresponding $[\text{Ar}]3d^5$ electronic configuration, where the maximum exchange between pairs of parallel-spin electrons significantly reduces the Coulombic potential energy. A manifestation of the stability of this configuration is the extraordinarily high Mn III ionization energy.[317] It is worth noting that this charge compensation mechanism likely takes place for highly dispersed Mn structures in contact with the Co surface like those considered here, and would probably be greatly reduced for larger multi-layer Mn conglomerates, where the oxidation state would be more rigidly linked to the stoichiometry.

Lastly, we point out that the results reported here are in agreement with previous experimental studies that measured predominantly divalent Mn species both after activation and during FT.[98, 101, 312] Yet, we note that this experimental observation does not provide information on the actual promoter phase in Co catalysts, since the Mn oxidation state does not necessarily correspond to the stoichiometry of the structures.

5.2.7. Conclusions

In this section, we shed light on several aspects regarding the Mn promotion of Co catalysts. The phase diagrams revealed that regardless of loading, particle size and crystal phase, the Mn structures are hydroxylated under FT conditions, with stoichiometries varying between $\text{MnO}_2\text{H}_{0.5}$ and MnO_2H . On the other hand, due the higher T and lower $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ ratios during reduction, the promoter is predicted to be in the MnO – $\text{MnO}_{1.5}$ state in the activated catalyst. Furthermore, the calculated ΔG^f , that are lower or comparable to that of bulk MnO , indicate that the Mn structures are highly stable under FT conditions. The fact that the most stable Mn phases are very close in energy, with differences often lower than 0.1 eV / Mn atom, underscores that the Mn structures can easily rearrange under reaction conditions, which might be linked to their catalytic activity.

The ΔG^f of the Mn structures is, however, loading dependent, as increasing Mn coverage significantly reduces their stability. Despite being observed for all the Mn phases, this effect

is more pronounced for the formally more oxidized ones, for which strong electrostatic repulsions and structural rigidity hinder agglomeration. The loading-dependent stability of Mn also originates by its preferential binding to the LCS on the Co NPs. As these become extensively covered with small Mn additions, further loading increase causes the formation of less stable structures adsorbing on the NPs terraces. We argue that the preferential Mn coverage of the Co LCS is a key hint to understanding the promotional effect. The increased TOF and C_{5+} selectivity of the promoted catalysts, in fact, suggest that Mn is not simply blocking the Co LCS, that are those responsible for CO dissociation. A possible promotional mechanism is one in which, while blocking some LCS, Mn is also promoting those that are adjacent and remain available for CO adsorption. Alternatively, a full blockage of the LCS by Mn would imply a promotion of the adjacent terrace sites, in which case a transition from direct to H-assisted CO dissociation would likely take place.[19, 53, 63, 111, 318] While this will be investigated in the next section, it is for now postulated that the electronic promotion of Mn might come from the facile rearrangement of the O and OH Mn ligands, that could enhance hydrogenation reactions as well as facilitate CO dissociation via O vacancy formation - filling cycles. Under the assumption that C-C coupling occurs on the Co LCS while the terraces mainly contribute to methanation,[177] a further hypothesis that we put forward is that Mn might prevent the diffusion of the C monomers from the LCS to the terraces, thus increasing the yield of C_{5+} products. Additionally, by anchoring to the LCS, Mn likely prevents their detachment and hence sintering by Ostwald ripening, which we have modeled in the previous chapter considering Co subcarbonyl formation from low-coordinated CN = 6 atoms. This hypothesis aligns with a recent experimental work that observed that the Mn-promoted catalyst sintered significantly less than its pristine counterpart.[58]

Furthermore, we could retrieve the expected oxidation state of Mn in our models, that was shown to always +2 regardless of loading, stoichiometry and NP structure. We ascribed this to a charge compensation mechanism in which the Co surface donates electrons to the promoter, allowing Mn to maintain the particularly favorable high-spin $3d^5$ electronic configuration. This aligns with experimental observations that report predominantly Mn^{2+} both in the activated and operating catalyst.

Lastly, we observed that neither particle size nor the crystal phase considerably alter the structures and the stability of Mn, as similar results were obtained across the different NP models.

To summarize, we have used a combination of sophisticated computational techniques to produce a holistic theory of Mn structures decorating Co NPs. We believe that this is the most advanced theoretical characterization of this system to date, as it accounts for several effects that are typically neglected, both because they require modeling length scales that are untreatable with DFT but also due to the lack of realistic starting NP models. In particular, we built upon the methodology established in Chapter 3 by optimizing the Mn structures over the NP models obtained from the MC simulations. Notably, this allowed us to consider the complexity of NP surfaces, yielding a more faithful representation of reality with respect to what is routinely done. The use of NP slabs, additionally, made it possible to directly link the number of simulated Mn atoms to the experimental promoter

loading and therefore to outline its effect on Mn speciation and stability, which cannot be unambiguously done when periodic surfaces are considered instead. Furthermore, conducting our investigation across three different NP models enabled us to take into account the effects of Co particle size and crystal phase, that are crucial given the structure-sensitivity of the FT synthesis and the coexistence of fcc and hcp-Co NPs in the catalyst. Additionally, the use of a GA optimization powered by a MLP ensured a comprehensive and yet relatively fast probing of the PES, reducing user bias while leveraging the computational speedup coming from recent advances in the field. In conclusion, we argue that this study stands as a testimony of the transformation that computational catalysis is currently undergoing, demonstrating how the combination of previously elaborated techniques with increased computing power is pushing the boundaries of what can be achieved with theoretical calculations.

5.3. Mn electronic promotion

5.3.1. Introduction and Methods

Scope. Having extensively characterized the structures of Mn and their interactions with Co NPs, our goal now is to investigate the electronic promotion of Mn, i.e. how it affects the FT reaction network. This task was carried out in collaboration with our colleagues at **Helmoltz Zentrum Berlin**, whose work is gratefully acknowledged in this thesis. In particular, MSc. **Pinar Sakoglu** carried out the experiments that we approach to describe here under the supervision of Dr. **Catalina Jiménez** and Dr. **Marcus Bär**. The results presented in this section are included in the following publication:

Sakoglu, P.; **Sireci, E.**; Frisch, J.; Zhong, T.; van der Merwe, M.; Hoffman, J.-A.; Starr, D.; Vinogradov, N.; Jones, R.; Shavorskiy, A.; Studt, F.; van Steen, E.; Bär, M.; Jiménez, C. E. CO Pulse Enabled Time Resolved In-Situ Investigation on the Chemical Structure of Co(0001) Fischer-Tropsch Model Catalysts Under Relevant Reaction Conditions. **2026**. *In Preparation*.

The experiments were carried out on Co(0001) single crystals, that were cleaned beforehand via Ar sputtering and annealing cycles. The samples were further annealed at 593 K to generate defects on the surface. FT synthesis was conducted at 493 K using a continuous H₂ flow and CO gas pulses at the HIPPIE beamline, where the surface intermediates evolution was monitored via near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). The total pressure in the system was 1.8 mbar. Approximately a 2 Å Mn layer was deposited on one of the sample, whose properties were compared to a pristine one. STM images were collected in ultra-high vacuum at 110 K at the MAX IV facility in Lund, Sweden. The STM images of the Mn-promoted sample presented showed that, after Mn deposition and annealing, Mn forms triangular motifs on the Co surface, which will be used as basis to construct our computational models. Furthermore, the C 1s X-ray photoelectron (XP) spectra recorded during FT both for the pristine and Mn promoted display significantly stronger peaks associated to $-C_xH_y$ on the Mn-promoted sample,

indicating a lowering of the barrier for CO dissociation, as previously postulated.[98, 101] The O 1s XP spectra additionally showed that the peaks assigned to adsorbed OH and H₂O are more intense in the presence of Mn, which mirrors the observations for the C 1s XP spectra as these species are likewise products of CO dissociation. On the other hand, this observation might also be linked to adsorbed OH and H₂O on the Mn structures. Lastly, near-ambient pressure X-ray absorption spectroscopy (NAP-XAS) experiments revealed that both Co and Mn did not change their oxidation states prior and after reaction, as they maintained metallic and +2 states, respectively.

In this section, we will attempt to elucidate the reaction mechanisms of CO dissociation and O removal both on Mn-promoted and pristine Co(0001) while making sure that our models are consistent with the experimental observations reported here.

Methods. The experimental STM images show that on Co(0001) Mn forms triangular motifs, which we reproduced with our theoretical models. To do so, we extracted one (111) plane from the bulk MnO crystal that was cut to obtain a triangular cluster composed of 6 Mn atoms with each side of approximately 1 nm. Even though this is significantly smaller than the structures observed via STM, we argue that this set up represents an optimal compromise between faithfulness to experiments and computational cost. We considered a $\sqrt{7} \times \sqrt{7}$ R19.1° unit cell and a only one k-point for the sampling of the Brillouin zone. The other DFT settings were the same as those used in the previous sections and chapters. TS search was carried out with the improved dimer method for the direct and HCO pathways for CO dissociation as well as for the O removal reaction. The CI-NEB method was used for TS identification in the pathway for CO dissociation via the COH intermediate.

To estimate the O content of the triangular motif under experimental conditions, we elaborated a simple algorithm, depicted in Figure 5.15, that identifies the GM of the Mn structures with O content varying between 6 and 13 atoms. The starting point of the algorithm is the fully oxidized Mn cluster (Mn₆O₁₃), that is sent to the inner loop. Here, only one of the 13 O atoms is removed, the resulting structure is relaxed with the fine-tuned CHGNet model and its energy is evaluated via a DFT single-point (SP) calculation; this operation is then repeated for all the O atoms. At the end of the inner loop, the GM with stoichiometry Mn₆O₁₂ is stored and used as the starting point for the next cycle. We carried out as many cycles as needed to obtain the GM of the Mn₆O₆ structure. In total, 76 structures were screened throughout the algorithm execution.

A similar algorithm was employed to estimate the H content of the triangular motifs. We start with a previously obtained GM structure with stoichiometry Mn₆O_x, that is sent to the inner loop. In a similar fashion as for the O content, here one H atom is added next to the first O atom, the resulting structure is relaxed with the tuned MLP and its energy is evaluated with a DFT SP calculation. We repeat the operation for all the O atoms in the structure and extract the GM for the stoichiometry Mn₆O_xH, which is subsequently used as starting point for the next cycle. We carried out as many cycles as needed to reach the GM for the fully hydroxylated structure with stoichiometry Mn₆O_xH_x. It is worth noting that this algorithm was carried out for the O contents ranging between 6 and 12 atoms, and hence a total of 335 structures were calculated throughout the optimization of the H content.

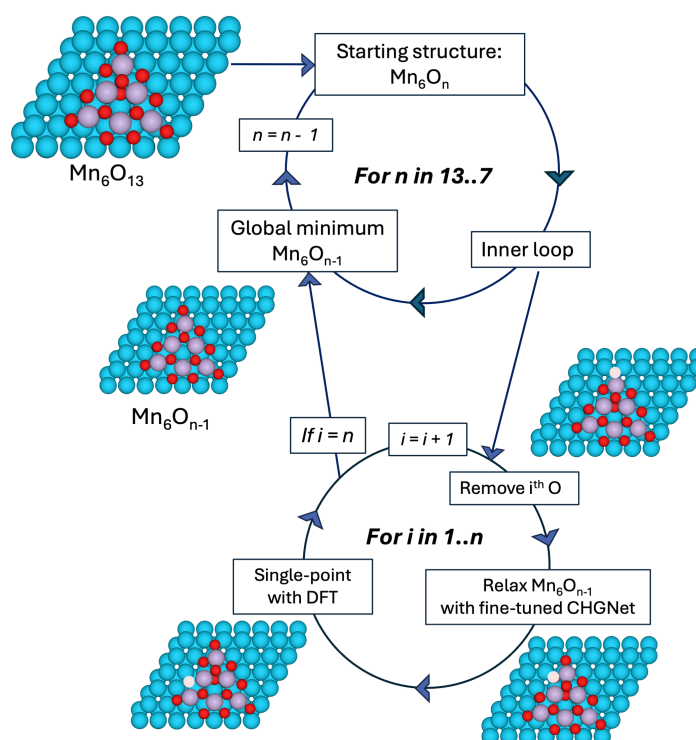


Figure 5.15.: Graphical depiction of the algorithm employed to retrieve the global minima of the triangular Mn islands on Co(0001) with different O contents.

5.3.2. Phase diagrams

In Figure 5.16 we present the phase diagram that outlines the relative stabilities of the Mn₆O_x structures with different O contents at T = 492 K and varying X_{CO} (and thus p_{H₂O}/p_{H₂} ratios). Under experimental conditions, for which it was estimated a X_{CO} of 1%, the five most stable structures that range between Mn₆O₇ and Mn₆O₁₁ are found within a very narrow energy window of roughly 0.2 eV (19 kJ/mol). This highlights that the triangular motifs are likely highly flexible during reaction conditions as they can easily adsorb and desorb O atoms. This is consistent with our predictions for the Mn_xO_yH_z structures on Co NPs presented in the previous section, where we showed that the different Mn phases are often close in energy. Additionally, we observe that the marked structural flexibility of the triangular motifs would be maintained even under industrial FT conditions (X_{CO} = 75%), where we predict the four most stable structures ranging between Mn₆O₉ and Mn₆O₁₂ to be found within roughly the same narrow energy window.

From the snapshots of the different identified GMs (Figure 5.17) it is shown that there is a regularity in the order of removal of the O atoms. In particular, with decreasing O content starting from the Mn₆O₁₂ GM, first one O atom is removed from each side of the triangle, resulting in three alternating O vacancies on the Mn₆O₉, and subsequently the remaining three oxygens located on the sides are removed. This indicates that the oxygens located on the sides are more easily removed than those located on the corners and in the inner regions of the Mn structures.

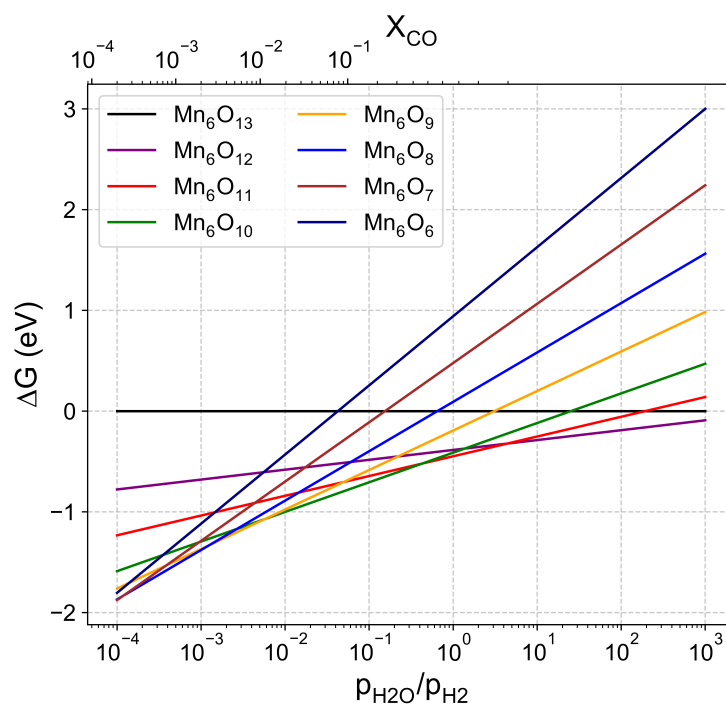


Figure 5.16.: Phase diagram showing the stability of the triangular Mn motifs with different O content. All the energies are referred to the fully oxidized Mn_6O_{13} structure.

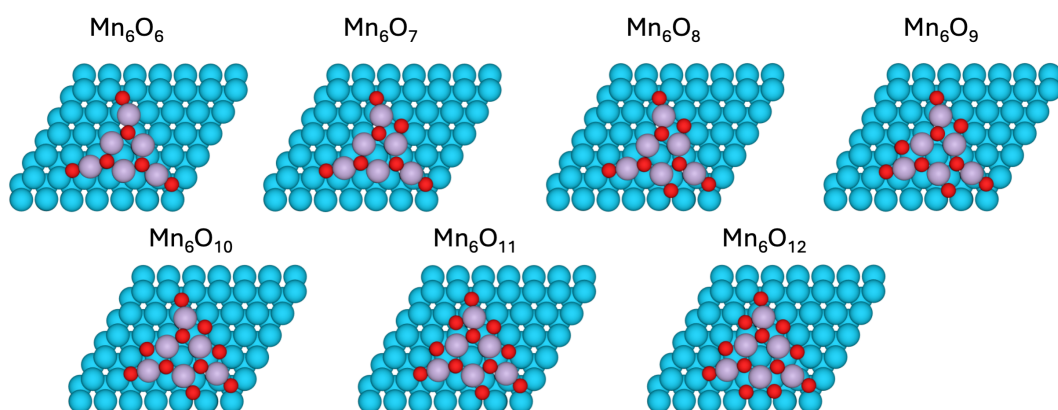


Figure 5.17.: Snapshots of the identified GM structures of the triangular Mn motif with varying O content.

In Figure 5.18, we present the phase diagrams showing the relative stabilities under reaction conditions of the different GM structures with increasing H content. Notably, up to the Mn_6O_9 motif, the dehydroxylated structure is always the most stable, and even if for the higher O contents the structures with one or two hydroxyl groups become more stable, they are still very close in energy to the fully dehydroxylated one. Hence, we conclude that, under reaction conditions, the Mn motifs will mostly be dehydroxylated. We note, however, that the hydrogen content in the structures depends both on the $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ ratio and the absolute value of p_{H_2} in the gas feed, that in the reference experimental setup is roughly four orders of magnitude lower than under industrial FT conditions. Therefore,

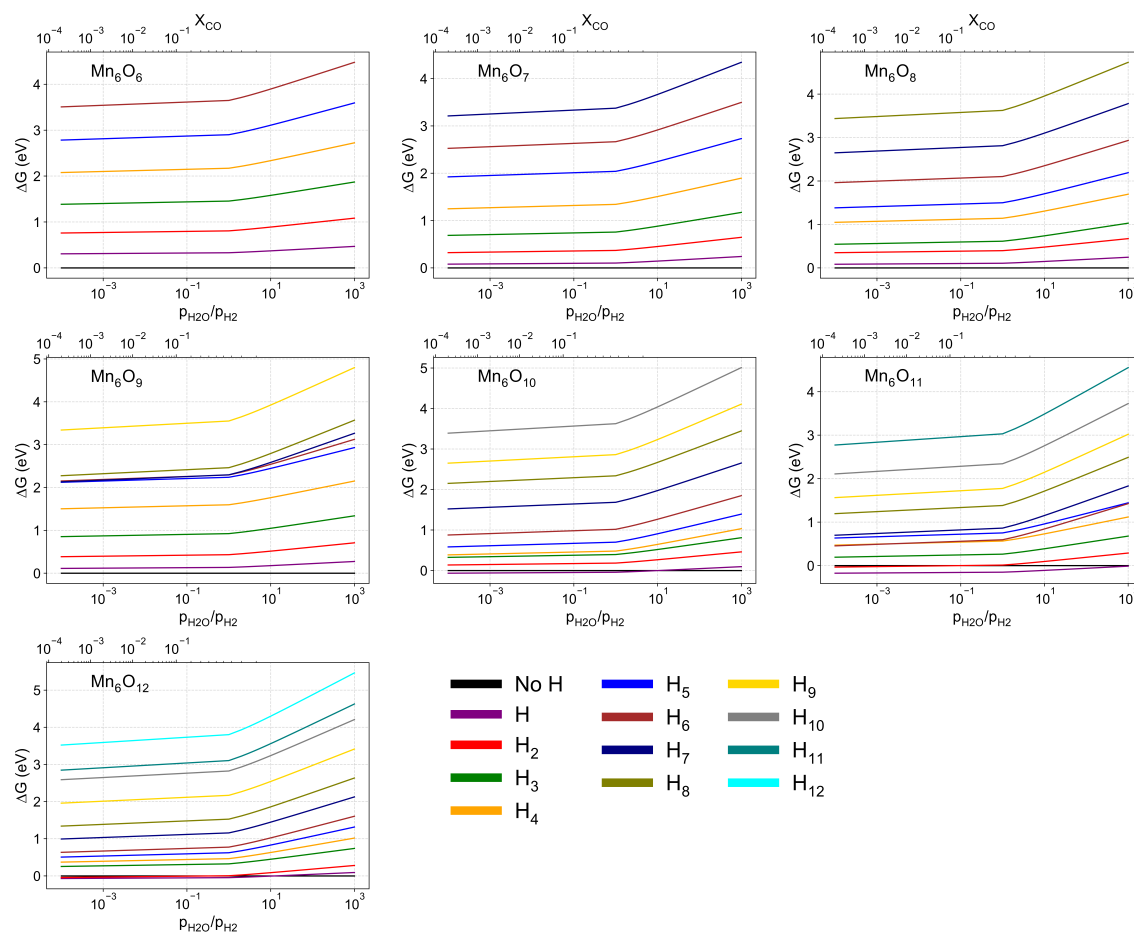


Figure 5.18.: Phase diagrams showing the stabilities of the triangular Mn motifs with different degrees of hydroxylation. Each diagram corresponds to a single O content, and all energies are referred to the fully dehydroxilated structure.

we ascribe the low degree of hydroxylation of our structures to the low pressure employed in the experiments. Besides, as shown in the previous section, our calculations predict that Mn structures on Co NPs under industrial FT conditions will have a certain degree of hydroxylation. We note that, with increasing O content, hydrogen adsorption becomes more and more favorable. For instance, the ΔG of the structure with six hydrogens progressively drops from roughly 3.5 eV for the Mn_6O_6 structure to just approximately 0.6 eV for the Mn_6O_{12} . This can be tentatively linked to the tendency of Mn to retain its divalent oxidation state, as the increasing negative charge due to the growing coverage by O anions tends to be balanced by electron donation both from the Co surface and H atoms rather than from Mn itself. Lastly, we note that the Mn motifs appear rather flexible also in terms of H content, as evidenced by the fact that, the more so with increasing O content, several structures with different degrees of hydroxylation are often close in energy to the most stable one.

In light of the results presented here, in the remainder of this section we will consider CO dissociation and O removal reaction pathways on the Mn_6O_8 and Mn_6O_9 triangular motifs,

respectively, that were shown to be among the most stable Mn structures on Co(0001) under reaction conditions. We note that the average Mn oxidation states as predicted from the atomic magmoms for the Mn_6O_8 and Mn_6O_9 structures are +2.2 and +2.1, that aligns with the experimentally reported +2 oxidation state of Mn on Co(0001).

5.3.3. Reactivity of Mn-promoted Co(0001)

CO dissociation. In Figure 5.19, we present the calculated reaction paths for the direct and H-assisted CO dissociation on the promoted and unpromoted Co(0001) surface. In the direct pathway, already described in Chapter 3, CO adsorption is followed by dissociation that occurs in just one step, yielding adsorbed C^* and O^* as end products. We observe slightly stronger CO adsorption in the presence of Mn, likely due to enhanced interactions between the oxygen of the CO molecule and the Mn atoms, that aligns with previous experimental and theoretical studies.[98, 99, 101, 122] In the H-assisted pathways, CO adsorption is followed by that of a H atom, that is energetically uphill because of the low p_{H_2} considered here. Under industrial FT conditions ($X_{\text{CO}} = 75\%$ resulting in $p_{\text{H}_2} = 2.4$ bar) H_2 adsorption would be stabilized by approximately 0.16 eV (per H atoms) and thus become roughly thermoneutral. Next, the adsorbed H atom hops on the C or the O of the adjacent CO molecule, forming a formyl or hydroxycarbonyl species, that dissociates either into HC^* and O^* or C^* and OH^* . We did not calculate the barrier for HCO^* formation because it is typically very shallow and much lower than that of dissociation,[111] while that of the COH^* formation on the pristine Co(0001) surface was not considered due to the fact that the following barrier for dissociation is already the highest among the investigated mechanisms and hence sufficient to rule out this pathway. We note that the formation of the hydroxycarbonyl species is predicted here to occur via disproportionation of a neighboring OH^* adsorbed on the corner of the triangular Mn motif.

Strikingly, all the investigated CO dissociation mechanisms are significantly enhanced for the Mn-promoted catalyst, that displays barriers that are lower by 0.49, 0.78 and 0.29 eV for the direct, COH and HCO mechanisms, respectively. In all cases, the reduction of the energy barrier is ascribed to the filling of the O vacancy on the side of the triangular Mn island by the dissociating O or OH groups, that leads to a stabilization of the TS in comparison to the clean Co(0001) surface. We note that, while in the direct and formyl routes the dissociated O^* binds to the hollow hcp site next to the Mn atoms, in the end state of the hydroxycarbonyl pathway the dissociated OH group binds to two Mn atoms but is detached from the Co surface. The relevant structures of the formyl pathway on the Mn promoted catalyst are shown in Figure 5.20.

Comparing the most favorable pathways for the two catalysts, that are in both cases the formyl routes, the calculated difference in barriers would correspond to roughly a three orders of magnitude difference in CO dissociation rate. This aligns with the experimental observation of significantly enhanced coverage of $-\text{C}_x\text{H}_y$ species on the promoted sample and corroborates the hypothesis that Mn enhances CO dissociation. We note that this hypothesis alone would be sufficient to explain the commonly observed promotional effects of Mn, i.e. increase in TOF and C_{5+} selectivity, with the latter being explained by the higher

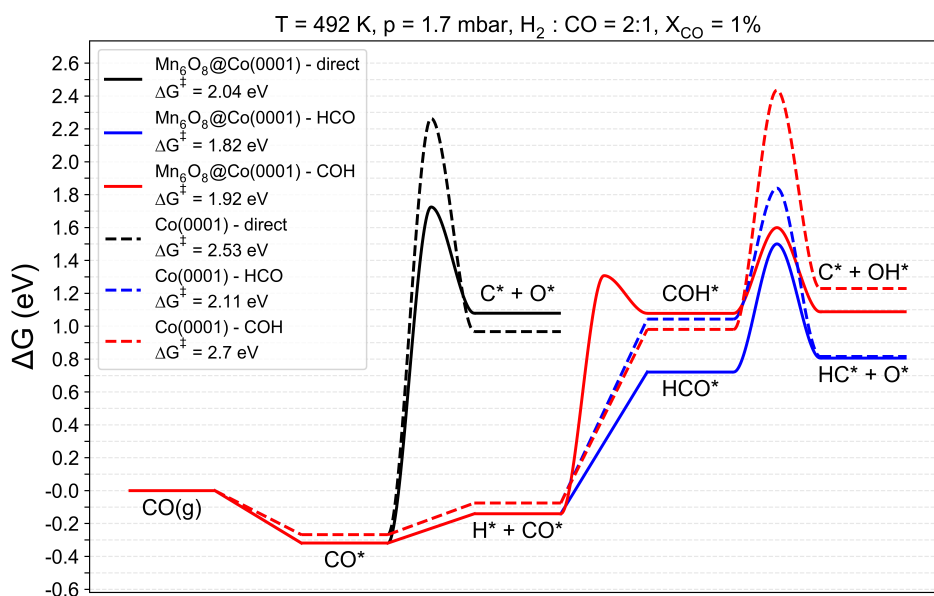


Figure 5.19.: Reaction diagram of direct and H-assisted (both via the HCO and COH routes) CO dissociation on promoted and unpromoted Co(0001).

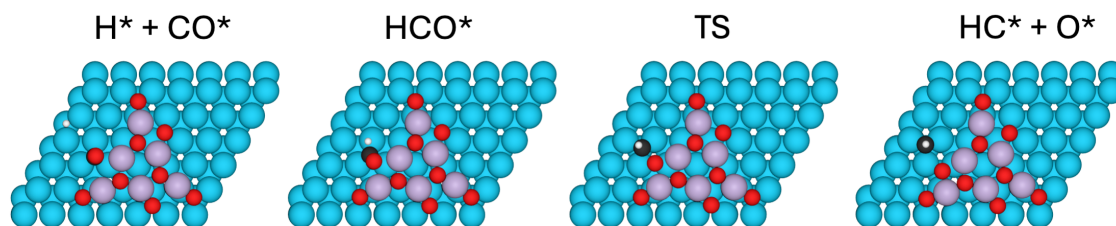


Figure 5.20.: Snapshots of the main reaction intermediates throughout the formyl CO dissociation pathway.

C coverage due to enhanced CO dissociation. Interestingly, while on the unpromoted catalyst the barrier of the formyl route is by far the lowest, in the presence of Mn the barrier of the hydroxycarbonyl pathway is only 0.1 eV higher. Given the inherent uncertainty of the calculations, we argue that both mechanisms likely contribute to CO dissociation. Lastly, we note that, given the thermoneutrality of H adsorption, the calculated barrier for CO dissociation via the formyl route on the promoted Co(0001) surface would become approximately 1.65 eV under industrial FT conditions. This is comparable to the barriers of direct CO dissociation on several LCS presented in Chapter 3, and indicates that on Mn-decorated Co NPs the promoted terrace sites might contribute to the overall CO dissociation rates.

O removal. The previously presented reaction mechanisms rely on the presence of an O vacancy on the side of the triangular Mn motif. To ensure that these are indeed viable pathways, we need to investigate how easy it is for the vacancy to form. In other words, to obtain a complete picture of the catalytic cycle proposed here, it is necessary to also consider the active site regeneration step, that must occur via O removal. In Figure 5.21, we present the relative reaction diagrams on the pristine and Mn-promoted catalysts. The

mechanism is proposed to occur via two subsequent hydrogenations of the adsorbed O^* atoms, that yield a weakly bound H_2O molecule that readily desorbs.

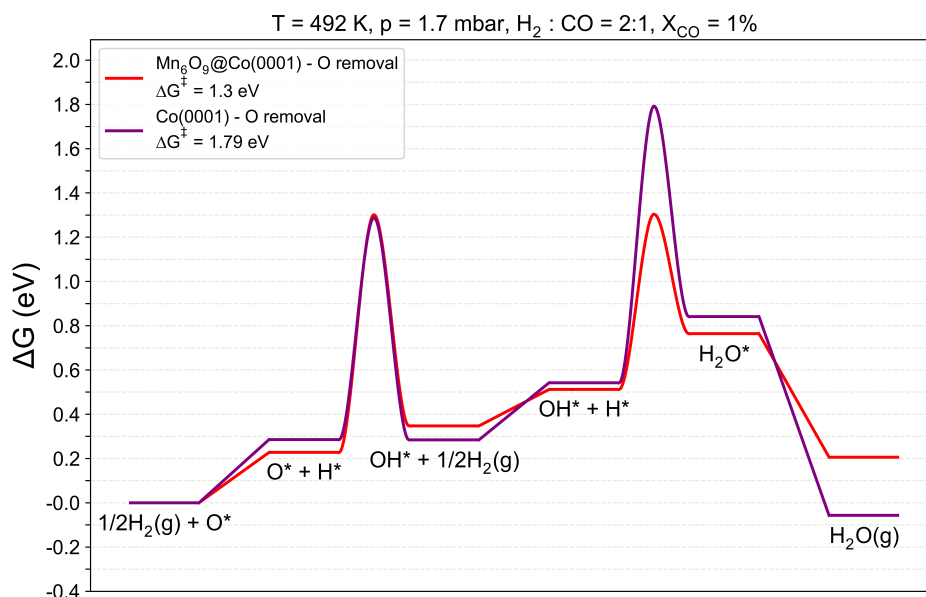


Figure 5.21.: Reaction diagram of O removal on promoted and unpromoted Co(0001).

While the first hydrogenation is energetically almost identical for the two catalysts, we note that the second hydrogenation is more facile in the presence of Mn by almost 0.5 eV, leading to an overall reaction barrier of only 1.30 against 1.79 eV for the unpromoted surface. The subsequent water desorption is energetically downhill in both cases, but significantly more so on the clean Co(0001) surface ($\Delta G = -0.9$ eV) than on the Mn-promoted one ($\Delta G = -0.57$ eV). Intuitively, it could be thought that for the same reason that the Mn structure enhances CO dissociation, i.e. by stabilizing the dissociating O, it should also hinder O removal. Nonetheless, we observe that kinetically the O removal is drastically faster on the Mn-promoted catalyst than on the pristine one. The key reason for this lies in the particularly favorable configuration of the second TS on the triangular Mn motif. Following the first hydrogenation, in fact, the adsorbed OH group binding to two Mn atoms shifts upwards with respect to the Co surface, from which it detaches. From this position, it is considerably more favorable for the OH ligand to bind to the second H atom adsorbed on Co with respect to when both species are located on the metal surface, which is the case in the absence of Mn. This is illustrated in Figure 5.22, where we present snapshots of the different stages of the O removal from the Mn triangular motif. Here, we observe that the TSs relative to the two hydrogenation steps are rather different, as the first one, characterized by a significantly higher barrier, involves O^* and H^* adsorbed on Co, while the second displays H^* adsorbed on Co being captured by the OH group above it.

We note, however, that our initial intuition is confirmed from a purely thermodynamic standpoint, as the overall reaction free energy (derived by comparing the initial and final states) is slightly exothermic for the pristine Co catalyst, while it is moderately

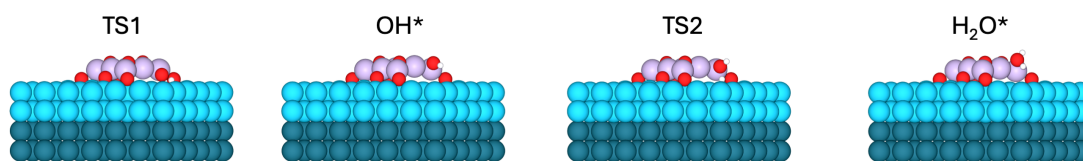


Figure 5.22.: Snapshots of the main reaction intermediates involved in the O removal process on the Mn-promoted Co(0001) terrace.

endothermic for the Mn-promoted one. We point out that the higher tendency of the Mn structure to retain adsorbed water with respect to the clean Co surface could be linked to the experimental observation of a more intense XPS peak relative to adsorbed water in the Mn decorated catalyst. Lastly, we note that, in both cases, the overall reaction barriers are significantly lower than those of CO dissociation, indicating that the latter is likely the rate-determining step.

Discussion. The experimental conditions considered here, however, are markedly different from those expected under industrial FT operation, on the one hand because of the significantly lower syngas pressure and X_{CO} , and on the other because the supported NPs employed in technical catalysts are structurally very different from the Co(0001) single crystals employed here. Hence, we must explain why we believe that our conclusions are of general character.

Let us first focus on how considering a typical industrial FT gas phase would affect our conclusions. Higher p_{H_2} would shift downwards the H-assisted CO dissociation barriers on both the promoted and pristine catalysts to a similar extent, hence not altering the trends outlined here. The higher $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ ratios due to higher X_{CO} , however, would significantly affect the energetics of the vacancy formation. In fact, while the starting Mn cluster in the catalytic cycle considered here (i.e. Mn_6O_8) is among the most stable structures for $X_{\text{CO}} = 1\%$, it would become roughly 0.5 eV less stable with respect to the most stable structures ($\text{Mn}_6\text{O}_{11}\text{-O}_{12}$) for $X_{\text{CO}} = 75\%$ as shown in Figure 5.16. Nonetheless, any initial energy penalty associated to vacancy formation would be readily compensated by CO adsorption in place of O^* , that would become more favorable by approximately 0.33 eV ($p_{\text{CO}} = 0.6$ mbar and 1.5 bar under reaction and industrial conditions, respectively) due to the higher syngas pressure. Hence, the purely thermodynamic destabilization of the O vacancy is unlikely to play an effect on the reaction mechanism. We can now take the reaction diagram of Figure 5.21 as reference to discuss the effects of the kinetics. Considering the promoted catalyst, both hydrogenation steps would shift downwards in energy by roughly 0.16 eV due to the higher p_{H_2} . The final H_2O desorption step, on the other hand, would shift upwards by approximately 0.6 eV, considering that the estimated reaction conditions yield $p_{\text{H}_2\text{O}} = 0.6$ Pa while industrially we would expect $p_{\text{H}_2\text{O}} = 5.0$ bar. This would be just enough to make the step approximately thermoneutral and would thus not affect the overall reaction barrier, that would actually decrease by 0.16 eV and become only 1.14 eV, that is vastly accessible at 492 K. Having demonstrated that CO dissociation would be equally facilitated on the promoted and unpromoted catalyst and that O removal would not become rate

determining, we can hence conclude that even in a industrial FT gas phase Mn promotion would enhance CO dissociation.

Regarding the issue of considering Co(0001) instead of NPs, we argue that the Mn structures predicted in Section 5.2 are qualitatively rather similar to the models considered here, as both consist of monolayer patches adsorbing on the Co surface. Nevertheless, we have shown that the energetics of CO dissociation are drastically different on the LCS, abundant on NPs, with respect to Co terraces. We argue, however, that is unlikely that the Mn promotional mechanism would fundamentally change when Mn decorates Co NPs. As shown in the previous section, the Mn structures on Co NPs are likely highly flexible, similarly to what was found for the triangular motif investigated here. This was shown to be a key property determining their catalytic activity, that is enabled by the easiness of the vacancy formation–vacancy filling cycles. On Co NPs, we expect the barriers for CO dissociation to be further reduced with respect to those reported here due to the presence of the LCS, but speculate that the Mn-promoted LCS are more active than the pristine ones, thus still causing an overall enhancement of CO dissociation. On the other hand, the O vacancy formation might be less facile on the LCS than on the terraces, and the overall barriers might fall in a similar range as those for CO dissociation. Thus, while our predictions clearly indicate that on Co(0001) CO dissociation is by far rate determining with respect to O removal, the situation on Co NPs might be less clear cut, and it might be the case that the best promotional effect is obtained when an optimal tradeoff between the two mechanisms is achieved.

5.3.4. Conclusions

In this section, we have used synergistically experimental measurements and theoretical calculations to elucidate the electronic promotional mechanism of Mn on Co catalysts. In particular, our models were built to reproduce the experimentally observed Mn triangular motifs on Co(0001) and underwent further optimization to estimate their O and H content under reaction conditions. In the most stable identified configurations, Mn was found to be in the divalent state, in agreement with experiments.

Our calculations reveal that Mn significantly lowers the barrier for CO dissociation, explaining the higher coverage of $-C_xH_y$ species on the promoted catalyst reported experimentally. This was ascribed to the emergence of a particularly active site consisting of an O vacancy at the interface between the Mn cluster and the Co surface. The negatively polarized O or OH group coming from a dissociating (hydrogenated) CO molecule, in fact, favorably interacts with the vacancy adjacent to Mn^{2+} cations, lowering the energy of the TS with respect to the unpromoted catalyst. The vacancy formation, on the other hand, was predicted to be slightly endothermic but also characterized by very low kinetic barriers. This indicates that the identified active site can easily be regenerated, and demonstrates the coherence of the proposed vacancy formation-filling (or inverse Mars-van Krevelen) mechanism for CO dissociation.

To conclude, we note that, despite being conducted at rather different conditions from industrial FT, the experimental results reported here reproduced the main observations from studies that considered realistic conditions. Since our models largely align and explain these experimental observations, we argue that they can likely be extrapolated as a general theory of Mn electronic promotion.

Part III.

Concluding Remarks

In this thesis, several aspects of Co FT catalysts were theoretically investigated. We were able to characterize in detail the structures of Co NPs thanks to the novel DFT-MC methodology elaborated in Chapter 3. Due to the simplicity of the employed energy model and the use of a 3D lattice framework, it was possible to simulate metal NPs up to tens of thousands of atoms at a reduced computational cost. The resulting models were proven to be exceptionally informative, as we could include the effects of temperature, size and – with only minor model modifications – metal-support interactions. Via this method, we were able to overcome several limitations of the classical Wulff construction such as its size and temperature independency, the assumption of ideal NP surfaces and its inability to factor in crystal facets not previously specified by the user.

Having these realistic NPs models at our disposal, we could reach several "low-lying fruits" that were previously inaccessible. In particular, we showed in Section 3.2 that the surfaces of fcc metal NPs are more intricate than previously thought, as they display a constellation of different plausible active sites whose nature strongly depends on particle size. By probing their reactivities via direct CO dissociation barriers calculations, we identified low-coordinated sites (LCS) that are significantly more active than the most active fcc sites reported in the literature to date. Additionally, we showed that their surface concentrations drastically increase with particle size up to 10 nm, in agreement with the experimentally reported structure sensitivity of Co catalysts. Furthermore, the proposed classification scheme establishes new guidelines to faithfully represent fcc active sites based on particle size.

The DFT-MC approach could be elegantly modified to show how the structures and stabilities of Co NPs are impacted by the FT gas phase. This was done by translating CO ΔG_{ads} at realistic coverages into CN-specific energy corrections, that could then be straightforwardly included in the energy model. CO was shown to induce drastic surface reconstruction consisting of an increase of B5-A step sites at the expenses of (111) and (100) terraces. Inserted C atoms at the base of B5-A step sites was identified as the main drive for the observed reconstruction, whose high stability was rationalized based on the doubly aromatic character of square-planar C embedded in metal surfaces. Furthermore, CO adsorption was found to significantly reduce the NPs surface energies, hence profoundly altering the $\Delta\mu_{\text{Co}}$ vs. D_{Co} profiles. The obtained energy profiles were then employed in a rate equation modeling catalyst deactivation by Ostwald ripening. In these simulations, we additionally integrated NPs geometrical factors as well as $\text{Co}(\text{CO})_x$ species formation and diffusion energies, that were found to govern sintering rates. In particular, the high CO content of the migrating subcarbonyl species makes their formation energies highly sensitive to p_{CO} oscillations foreseeable within industrial FT operation, attested by the dramatic sintering acceleration when increasing p_{CO} from 1.5 to 5 bar. Additionally, the higher $\text{Co}(\text{CO})_x$ diffusion barriers on $\gamma\text{-Al}_2\text{O}_3$ determined significantly slower deactivation on this support as compared to anatase and rutile TiO_2 . The initial particle size distribution was also found to impact sintering. The mean initial D_{Co} had a large impact on deactivation rates, as the $\Delta\mu_{\text{Co}}$ profiles become steeper with decreasing particle size resulting in faster sintering. In comparison, the width of the initial distribution had a less prominent effect, even though narrower distributions are characterized by somewhat slower deactivation particularly in the initial stages of the simulations.

In Chapter 5, we finally focused on modeling Mn promotion of Co FT catalysts. Prior to diving deep into calculations, in Section 5.1 we established the optimal U_{eff} value to describe the reactivity of Mn oxides and additionally retrieved correlations between the formal Mn oxidation state and both its Bader charge and atomic magnetic moment, which were later used to align our models with experimental observations.

In order to untangle the complex Mn promotional effects, we needed to resort to more comprehensive computational models with respect to the state-of-the-art. Hence, we employed a GA powered by a MLP to predict low-energy Mn structures with different stoichiometries and loadings adsorbing on the previously obtained MC NPs models. We first built a comprehensive dataset of $\text{Mn}_x\text{O}_y\text{H}_z$ clusters adsorbed on different Co periodic surfaces, that was used to fine-tune the original CHGNet potential. The procedure ultimately yielded a potential with near-DFT accuracy at a fraction of the cost. By following this strategy, we could effectively model the complexity of realistic NP surfaces, accounting for the presence of defects and intersections between different facets, which is overlooked when periodic Co surface models are considered instead. Additionally, by considering different NP models, we could resolve the Mn-Co interactions with changing particle size and crystal phase. Finally, by relating the number of simulated Mn atoms to those in the Co NPs, we could unambiguously investigate the speciation of Mn in a loading range close to those reported experimentally. The calculated phase diagrams showed that while after reduction Mn is preferentially in the MnO - $\text{MnO}_{1.5}$ phases, the lower temperature and different gas phase during FT favors the formation of hydroxylated Mn structures. Increasing promoter loading was found to favor the formally more reduced phases and to significantly destabilize the Mn structures, indicating that they might eventually become more prone to binding to the support. Particle size and crystal phase did not largely affect the stability of Mn, that was predicted to be only marginally more stable on the hcp NP model than on the fcc counterparts. Mn was found to preferentially bind to the LCS on the NPs surfaces, which likely has significant implications for activity given the pivotal role of these sites on pristine Co NPs. This was additionally linked to the increased sintering resistance of Mn-promoted catalysts, as by covering the low-coordinated atoms the promoter might inhibit their detachment and suppress the formation of Co subcarbonyl species. Furthermore, we outlined the existence of a charge compensation mechanism according to which the Co NPs, acting as electron reservoirs, donate charge to the promoter clusters to keep Mn in the particularly favorable $2+$ electronic configuration, even when we would expect otherwise based on the Mn:O:H ratios. As mentioned above, these insights could have hardly been obtained by standard DFT calculations, which underscores how recent advances in the field are significantly enhancing the predictive power of theoretical calculations.

Finally, we elucidated the electronic promotion of Mn by carrying out theoretical calculations in synergy with experiments performed by our colleagues at Helmholtz Zentrum Berlin. In particular, we elaborated computational models consisting of triangular MnO_x motifs on $\text{Co}(0001)$, mimicking the experimental conditions and STM images. By calculating CO dissociation pathways on both the Mn-promoted and pristine $\text{Co}(0001)$, we found that Mn significantly lowers the CO dissociation barriers by generating particularly active sites consisting of O vacancies on the sides of the Mn clusters, where the $\text{C}-\text{O}^{\delta-}$

can favorably coordinate to the Mn^{2+} centers, lowering the energy of the transition state via a Lewis base-acid interaction. Our predictions aligned with experiments that observed enhanced $-\text{C}/-\text{C}_x\text{H}_y$ formation on the Mn-promoted crystals, which are direct products of CO dissociation. Furthermore, even though the Mn-promoted surface was found to have a higher thermodynamic tendency to retaining water, it was also predicted to offer a significantly faster kinetic pathway for O removal. Despite the experimental-simulation setup was relative to conditions rather far from industrial applications, we discussed the reasons why the main conclusions of this section could be extrapolated as a general theory of Mn electronic promotion.

There are, as expected, research questions that remain unanswered and that could be tackled in future studies. While in this thesis we carried out an in-depth characterization of the surface conformation of fcc-Co NPs, we acknowledge that in technical catalysts they coexist with a significant portion of hcp-Co that was indicated to be more active. Hence, a similar analysis as the one carried out in Section 3.2 applied to hcp-Co NPs could shed light on the reasons for the observed differences in performances between the two crystal phases, and particularly on whether the hcp phase simply possess a larger concentration of active sites or it presents particularly active ones that are absent on fcc-Co. Additionally, it could prove insightful to outline whether hcp-Co NPs obey similar structure sensitivity trends as those reported for their fcc counterparts. Moreover, Co NPs with stacking faults or mixed fcc-hcp domains can occur in real catalysts even though their structures have been hardly investigated to date, suggesting that there might be relevant surface sites that have so far been neglected. We note that our DFT-MC methodology could be easily adapted to model these systems by providing relevant grid files throughout the algorithm runs.

A further aspect of Co FT catalysts that has been overlooked in this thesis is the possible impact of poisons, of which Sulphur, Nitrogen and Chlorine are presumably the most relevant. This could be straightforwardly probed by comparing adsorption energies of these elements to that of Carbon on the different LCS, and could ultimately reveal the different poisons concentration thresholds that can be sustained by the catalyst without causing significant deactivation. Additionally, this could prove whether the different sites predicted in this thesis are available under typical industrial FT conditions or are blocked early on by strongly-adsorbing species.

There are likewise open questions regarding the Mn promotional effect. In particular, our models of Mn structures on Co NPs neglected possible surface reconstruction effects induced by Mn: due to the preferential binding of Mn to the LCS, the promoter could in fact cause a corrugation of the NPs surfaces, possibly increasing the concentration of the active sites which could contribute to the overall promotional effect. Furthermore, and perhaps more critically, the Mn structures were calculated in the absence of CO. During FT, however, the Mn clusters must compete for adsorption on Co with strongly binding CO molecules, that could likely displace the less stable Mn structures such as those on the terraces as well as constraining the ones strongly anchored to the LCS. Additionally, in this work we did not investigate the speciation and stability of Mn on the different support materials. This could lead to quantitative predictions regarding the proportions of Mn

covering the Co NPs and the support, and would make the link between experimental and simulated Mn loading more direct. Additionally, support modifications by Mn might affect the formation and diffusion of $\text{Co}(\text{CO})_x$ species and hence sintering dynamics, that could be an additional way in which Mn increases catalyst resistance. Lastly, in order to match the available experimental results, here we investigated the electronic promotion of Mn on Co(0001) terraces, even though on Co NPs the promoter preferentially binds to steps and kinks. Hence, calculations of relevant reaction steps at the interface between Mn clusters and Co LCS could be more relevant to technical catalysts, and would help verify whether the reported enhancement of CO dissociation and O removal by Mn for Co(0001) single crystals also holds for NPs.

To conclude, this thesis demonstrates how advanced atomistic modeling strategies can address the multiscale complexity of Fischer–Tropsch catalysis beyond conventional surface-science approaches. By integrating first-principles calculations with Monte Carlo simulations, machine-learning potentials, global optimization techniques, and kinetic modeling, it establishes a unified framework for understanding structure sensitivity, gas-phase-induced restructuring, catalyst deactivation, and promoter effects in cobalt-based FT catalysts. The methodologies and insights developed herein are broadly transferable and contribute to the rational design of more efficient and durable catalysts for sustainable aviation fuel production.

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A. Appendix

A.1. Appendix Chapter 3

Additional figures and tables from Chapter 3 are listed below.

	$\Delta H_{\text{rxn}} \left(\frac{\text{kJ}}{\text{mol}} \right)$
Exp. ^a	0.8
U = 0 eV	65.5
U = 1 eV	32.1
U = 2 eV	-11.8
U = 3 eV	-52.9
U = 4 eV	-92.6

Table A.1.: Reaction enthalpy ΔH_{rxn} of $\text{Co} + \text{H}_2\text{O} \rightarrow \text{CoO} + \text{H}_2$ as a function of the Hubbard parameter U .
^aExperimental references are taken from the NIST-JANAF thermochemical tables, 1985 version 1.0.

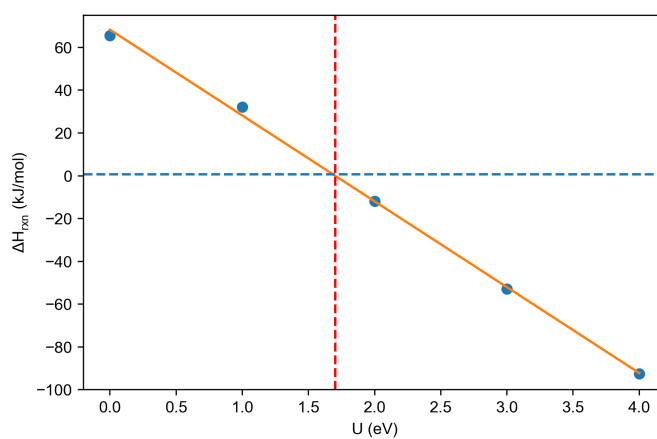


Figure A.1.: Calibration of the U value using the calculated values of Table A.1. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

Table A.2.: Specifications of the surfaces used to collect the data points of Figure 5.8 and to construct the Wulff particle.

Structure	# of Co atoms on the surface	Supercell	γ (meV/Å ²)
(111)	1 CN9	1x1	134
(100)	1 CN8	1x1	160
(110)	1 CN11, 1 CN7	2x1	155
(211)	1 CN10, 1 CN9, 1 CN7	3x1	155
(311)	1 CN10, 1 CN7	2x2	157
(111) – 1/9 ML vacancy	3 CN11, 2 CN9, 6 CN8	3x3	162
(111) – 1/3 ML vacancy	9 CN11, 6 CN6	3x3	203
(100) – 1/9 ML vacancy	4 CN11, 4 CN8, 4 CN7	3x3	183

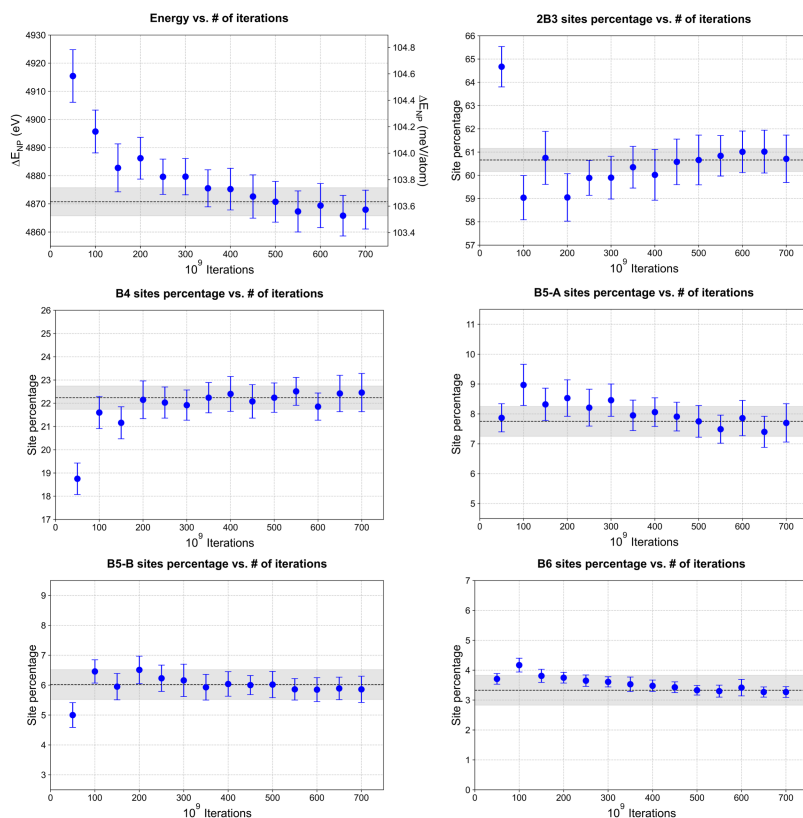
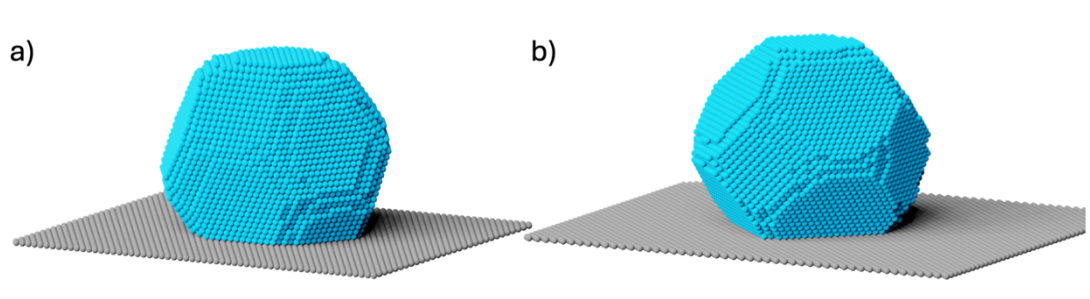
**Figure A.2.:** Average energy and site distribution collected over different runs with increasing number of iterations for a 10 nm nanoparticle. MAEs are reported as error bars, shaded areas indicate the employed convergence range. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

Table A.3.: Relative surface energies (γ) of the different terminations of the investigated oxide slabs.

Material	Termination	γ (meV/Å ²)
CoTiO ₃ (0001)	Reduced	0
	1 O	-31
	2 OH	-104
Co ₂ SiO ₄ (001)	Reduced	0
	3 OH	-11
	6 OH	-46
	3 O	-23
	6 O	31
	Dry	0
γ -Al ₂ O ₃ (110)	Dry	0
	1 H ₂ O	-15
	2 H ₂ O	-34
	3 H ₂ O	-50
	4 H ₂ O	-52
	5 H ₂ O	-47
CoAl ₂ O ₄ (110)	Dry	0
	1 H ₂ O	-22
	2 H ₂ O	-21
	3 H ₂ O	-45
	4 H ₂ O	-33

**Figure A.3.:** Snapshots of 8 nm Co NPs forming the a) Co (111) – SiO₂ (001) and b) the Co (100) – SiO₂ (001) interfaces. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

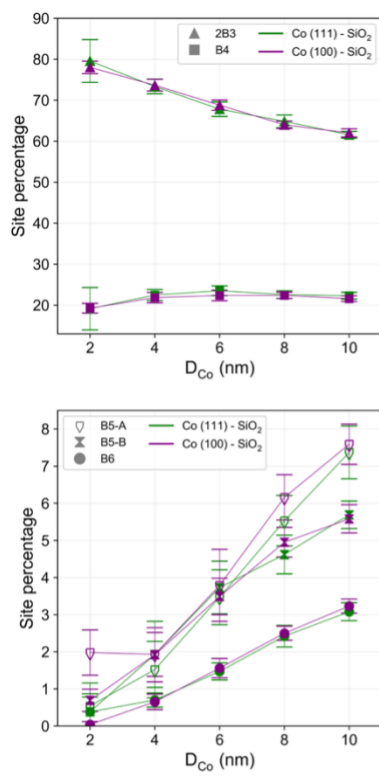


Figure A.4.: Site distribution analysis of Co NPs forming the the Co (111) – SiO₂ (001) and the Co (100) – SiO₂ (001) interfaces. Reprinted from Ref. [171] with permission. Copyright 2025 American Chemical Society.

Table A.4.: CO adsorption energies (ΔE_{ads} , eV) on the different low-coordinated sites (LCS) of fcc-Co nanoparticles, ZPE excluded.

Site	Top	Bridge	Threefold	Fourfold	Fivefold
Edge B2	-1.56	-1.46	–	-1.39	–
Edge B1	-1.50	-1.43	-1.32	–	–
Corner	-1.46	-1.44	–	-1.34	–
B5-B (110)	-1.48	-1.41	-1.43	–	-1.34
B5-A (211)	-1.45	-1.36	-1.43	–	-1.13
B5-B (221)	-1.50	-1.46	–	-1.28	-1.32
B5-A (311)	-1.42	-1.41	–	–	-1.09
B6 (321)	-1.52	-1.50	-1.41	-1.29	–
B5-A (331)	-1.38	-1.44	–	–	-1.21
B6 (641)	-1.44	-1.38	–	-1.37	-1.41
B5-A corner (100)	-1.39	-1.39	–	–	-1.39
B5-A corner (111)	-1.40	-1.42	-1.40	–	-1.39
B5-B corner (111)	-1.40	-1.42	-1.40	–	-1.17

A.2. Appendix Chapter 4

Additional figures and tables from Chapter 4 are listed below.

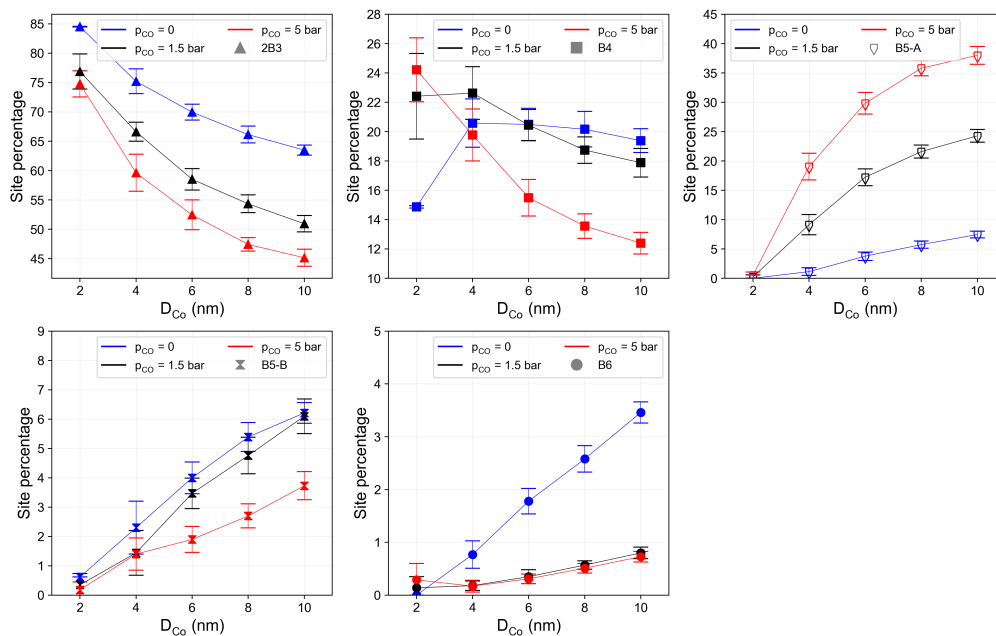


Figure A.5.: Site distribution analysis of the CoAl_2O_4 -supported NPs with increasing size and changing p_{CO} . Reproduced from [240] with permission from the Royal Society of Chemistry.

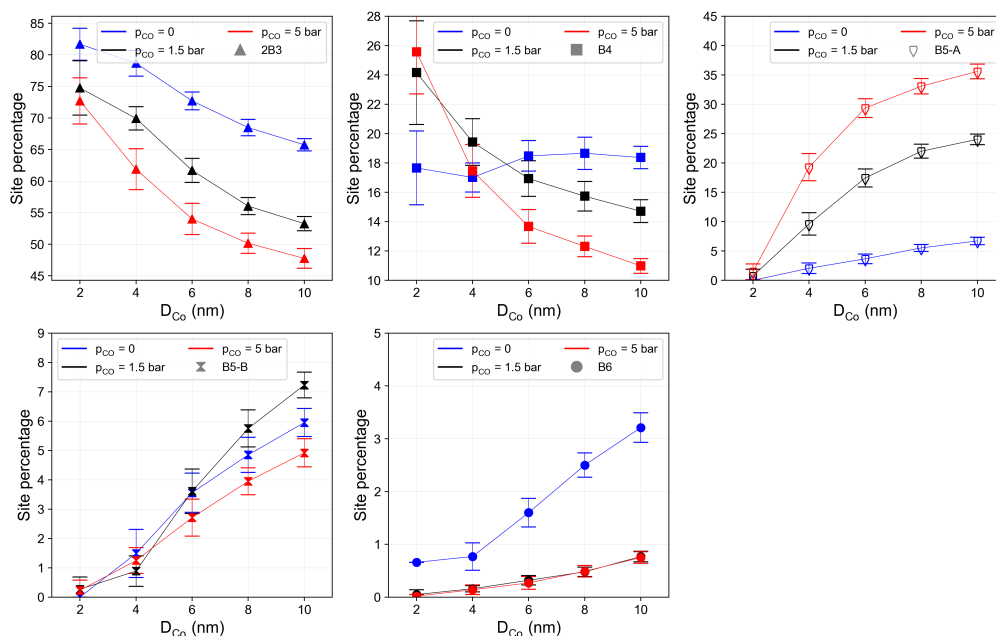


Figure A.6.: Site distribution analysis of the CoATiO_3 -supported NPs with increasing size and changing p_{CO} . Reproduced from [240] with permission from the Royal Society of Chemistry.

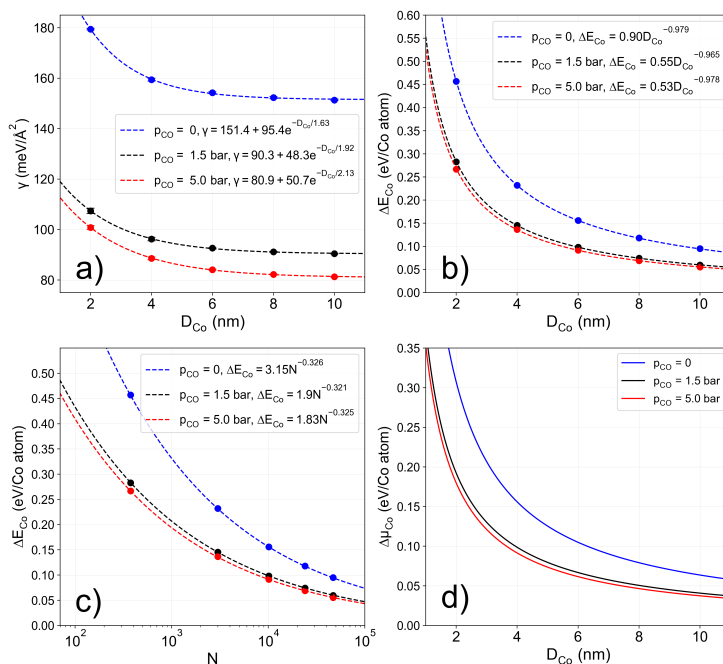


Figure A.7.: CoAl₂O₄-supported Co NPs a) surface energies with increasing D_{Co} and p_{CO}, b) average energy per atom ΔE_{Co} with respect to bulk Co with increasing D_{Co} and p_{CO} and c) with increasing number of atoms (N) and p_{CO}. d) Chemical potential of the free-standing Co NPs with respect to bulk Co Δμ_{Co} with increasing D_{Co} and p_{CO}. Reproduced from [240] with permission from the Royal Society of Chemistry.

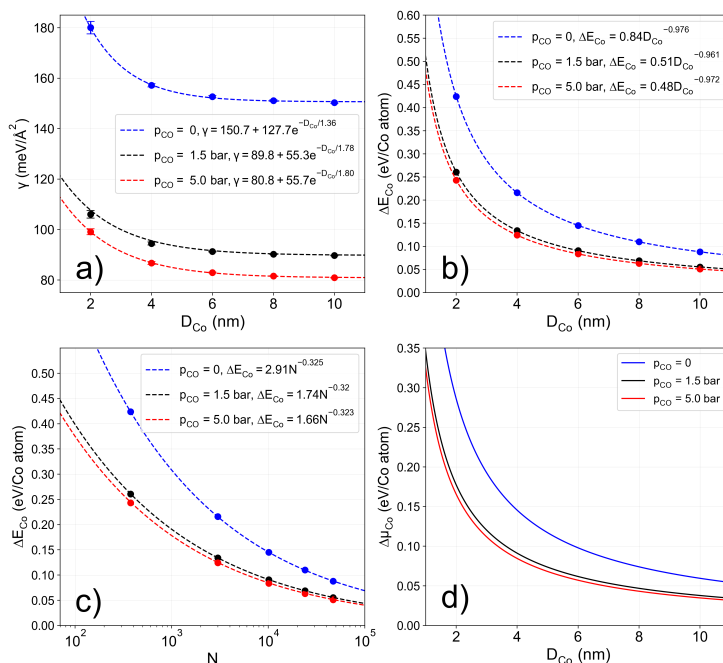


Figure A.8.: CoTiO₃-supported Co NPs a) surface energies with increasing D_{Co} and p_{CO}, b) average energy per atom ΔE_{Co} with respect to bulk Co with increasing D_{Co} and p_{CO} and c) with increasing number of atoms (N) and p_{CO}. d) Chemical potential of the free-standing Co NPs with respect to bulk Co Δμ_{Co} with increasing D_{Co} and p_{CO}. Reproduced from [240] with permission from the Royal Society of Chemistry.

A.3. Appendix Chapter 5

Additional figures and tables from Chapter 5 are listed below.

Table A.5.: Zero-point energies (ZPE), enthalpy changes from 0 to 298 K ($\Delta\Delta H^{0\rightarrow 298K}$), calculated standard entropies (S_{calc}^0) and experimental standard entropies (S_{exp}^0) of the investigated species. For solids, only the vibrational entropy contribution was considered in the calculated values.

Species	ZPE (kJ/mol)	$\Delta\Delta H^{0\rightarrow 298K}$ (kJ/mol)	S_{calc}^0 (J/(mol·K))	S_{exp}^0 (J/(mol·K))
MnO	8.2	8.5	53.8	59.0
Mn ₃ O ₄	40.1	23.9	143.5	165.6
Mn ₂ O ₃	27.7	17.3	101.8	113.7
MnO ₂	21.3	8.2	45.3	52.8
H ₂ O	55.1	10.0	187.9	189.0
H ₂	26.5	8.7	129.6	130.9

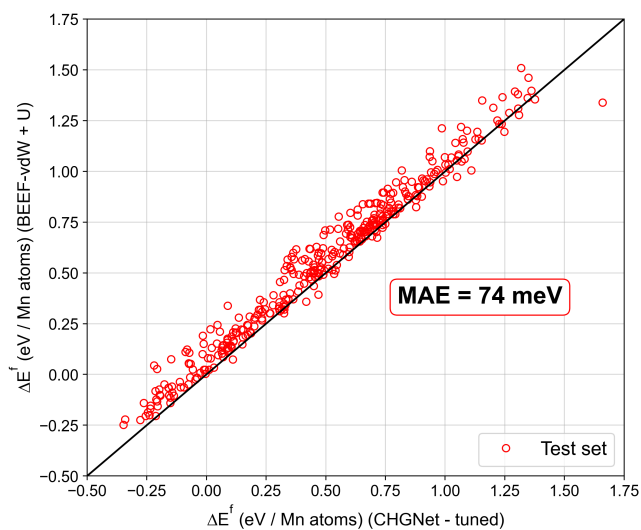


Figure A.9.: Parity plots of $\text{Mn}_x\text{O}_y\text{H}_z@hcp\text{-Co}$ clusters formation energies as defined in equation 5.5 calculated with DFT and the fine-tuned CHGNet MLP.

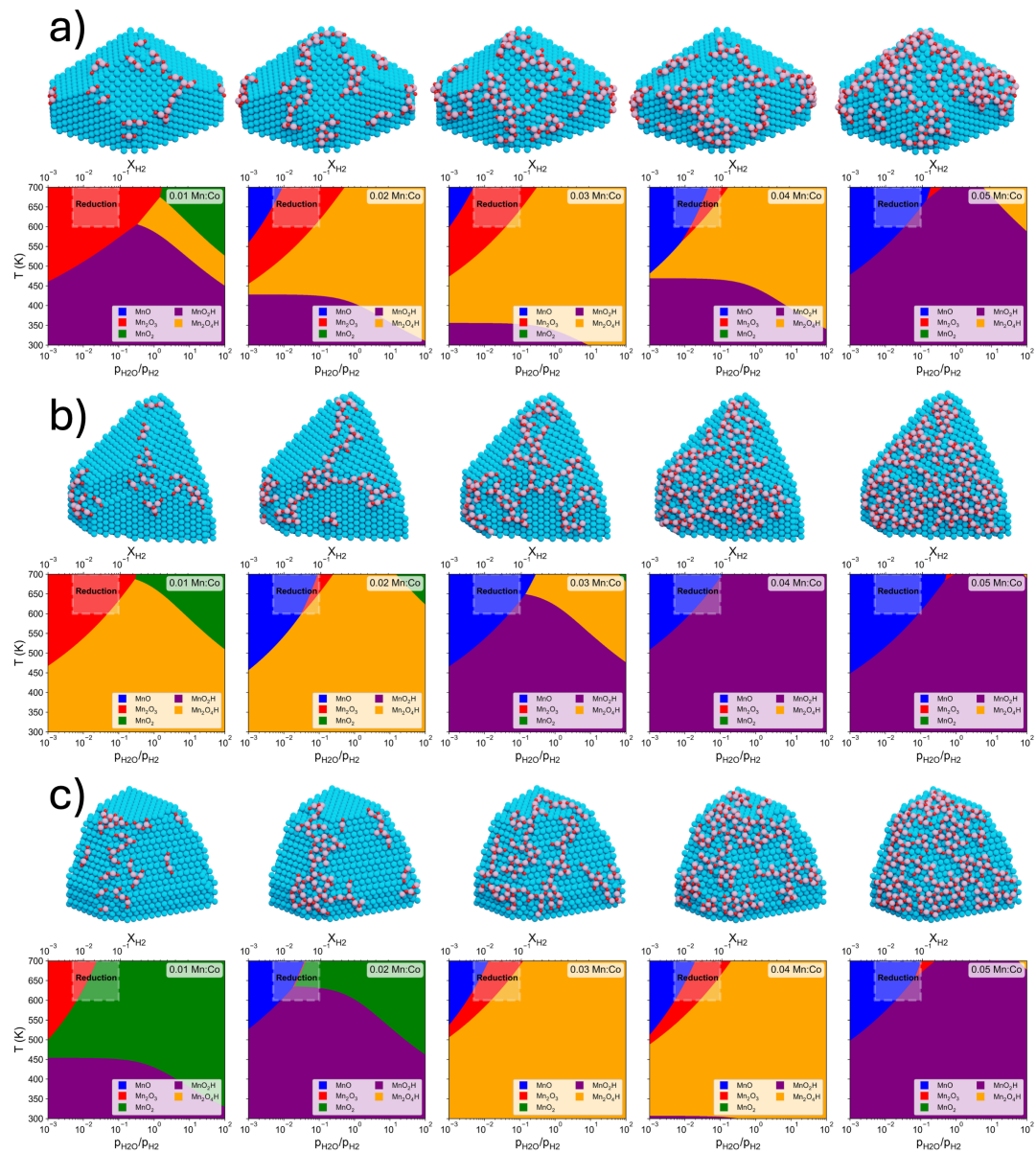


Figure A.10.: Phase diagrams calculated in a typical reduction gas phase ($p_{H_2} = 1.0$ bar) of Mn structures with loadings ranging from 0.01 to 0.05 Mn:Co on a) 6 nm fcc-Co NP slab, b) 8 nm fcc-Co NP slab and c) 8 nm hcp-Co slab. Snapshots of the most stable phases under FT condition are included above the respective phase diagrams.

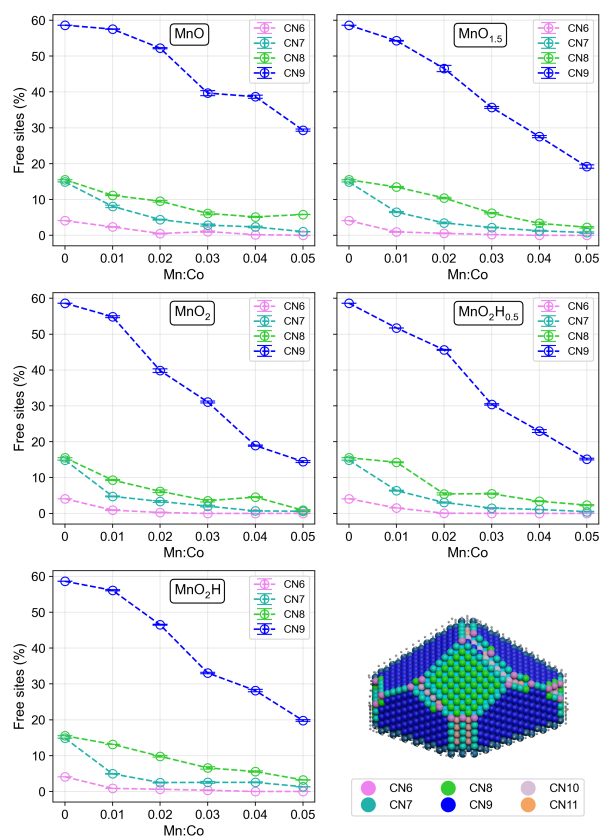


Figure A.11.: Percentage of free Co sites with different coordination numbers with increasing Mn:Co ratios for all the investigated Mn phases on the 6 nm fcc-Co NP model.

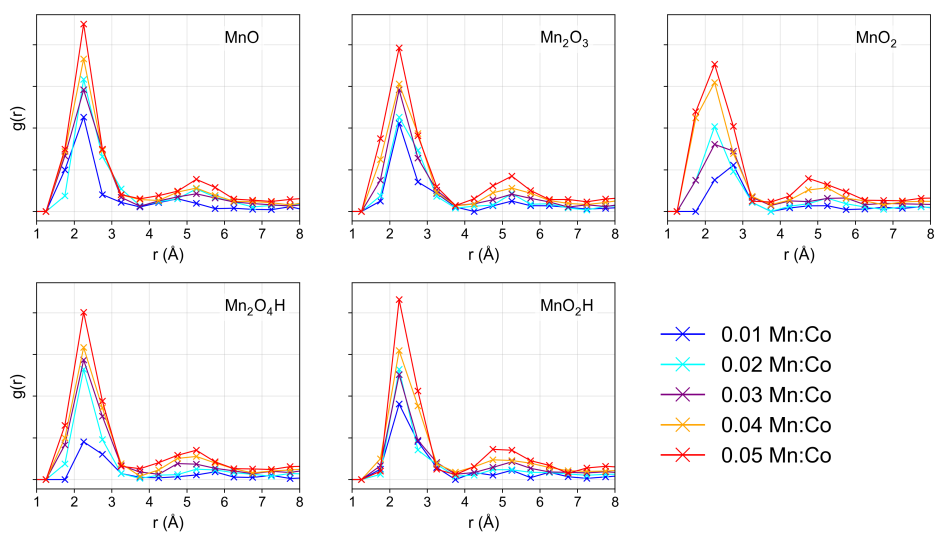


Figure A.12.: Mn-Mn radial distribution functions (g(r)) for the different Mn phases on the 8 nm hcp-Co slab with increasing loading.

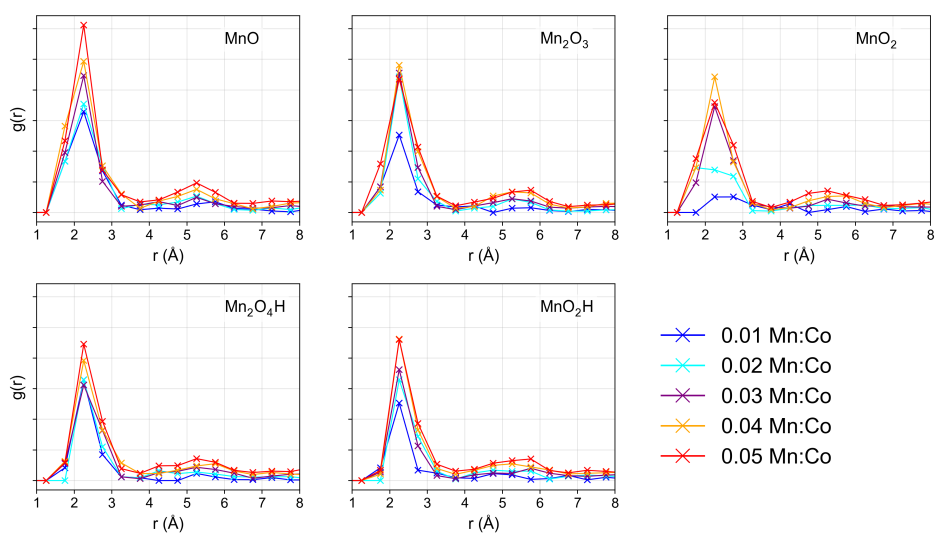


Figure A.13.: Mn-Mn radial distribution functions ($g(r)$) for the different Mn phases on the 6 nm fcc-Co slab with increasing loading.

List of Abbreviations

AtJ	Alcohol-to-Jet
CN	Coordination Number
CHGNet	Crystal Hamiltonian Graph Neural Network
DFT	Density Functional Theory
FT	Fischer–Tropsch
GA	Genetic Algorithm
HC	Hydrocarbon
HEFA	Hydrotreated Esters and Fatty Acids
HTFT	High-Temperature Fischer–Tropsch
kMC	Kinetic Monte Carlo
LCS	Low-Coordinated Sites
LTFT	Low-Temperature Fischer–Tropsch
MC	Monte Carlo
MLP	Machine Learning Potential
MSI	Metal–Support Interaction
NP	Nanoparticle
PES	Potential Energy Surface
PMC	Particle Migration and Coalescence
SAF	Sustainable Aviation Fuel
STEM	Scanning Transmission Electron Microscopy
TOF	Turnover Frequency
TPR	Temperature Programmed Reduction
TS	Transition State
WGS	Water-Gas Shift

ZPE Zero-Point Energy

B. Acknowledgments

Looking back at the past three years and a half, it is challenging to recollect my thoughts and remember all the people that helped me along the way. I apologize if my memory fails me and prevents me from mentioning someone that deserved to be acknowledged.

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Finally, to Natia, my love. Looking back, it is incredible what you sustained and did for me throughout the years. When I felt like I was alone in this world, you stood as a focal point giving me strength and a sense of security. No matter what I did (or did not do), you always came with your unconditional love, for which I will be forever grateful.

C. List of Publications

1. **Sireci, E.**; Grüger, T. D.; Plessow, P. N.; Sharapa, D. I.; Studt, F. Modeling the Shape and Stability of Co Nanoparticles as a Function of Size and Support Interactions through DFT Calculations and Monte Carlo Simulations. *The Journal of Physical Chemistry C* **2025**, 129 (29), 13232–13243.
2. **Sireci, E.**; Grüger, T. D.; Plessow, P. N.; Sharapa, D. I.; Studt, F. Modeling the Shape and Stability of Supported Co Nanoparticles under Fischer-Tropsch Conditions via DFT Calculations and Monte Carlo Simulations: Insights into CO-Driven Surface Reconstruction. *Catalysis Science & Technology* **2025**, 15 (22), 6703–6715.
3. **Sireci, E.**; Sharapa, D. I.; Studt, F. A Comprehensive Overview of Active Sites of Fcc-Co Nanoparticles and Their Role in CO Splitting—A DFT Study. *The Journal of Physical Chemistry C* **2025**, 129 (49), 21634–21641.
4. Zimina, A.; Fadlalla, M. I.; Potgieter, J.; Jimenez, C. E.; Ilica, R.; **Sireci, E.**; Sharapa, D. I.; de Oliveira, D.; Hsu, C.; Saraci, E.; Wolf, M.; Sakoglu, P.; Skaltsogiannis, A.; Zhong, T.; Bär, M.; Botha, T.; Moodley, D.; Claeys, M.; Studt, F.; Grunwaldt, J.-D. Comparison of Industrially Relevant Fischer-Tropsch Cobalt Catalysts Supported on Alumina and Modified Silica with Complementary In-Situ and Operando Characterization Methods. *The Journal of Physical Chemistry C* **2026**, 130 (10), 3676–3690.
5. Vermaak, V.; Cunningham, R. D.; Potgieter, J. H.; Botha, J. M.; van Steen, E.; Claeys, M.; Fadlalla, M.; Hoffman, J.-A.; Abdullah, S.; **Sireci, E.**; Studt, F.; Zimina, A.; Grunwaldt, J.-D.; Hsu, C.; Wolf, M.; Jiménez, C.; Sakoglu, P.; Moodley, D. Manganese-Enhanced Cobalt Catalysts for Fischer-Tropsch Synthesis: A Review of Structural and Electronic Promotion Effects. *Catalysis Science & Technology* **2026**, 16 (15), 1488–1530.
6. Hoffman, J.-A.; **Sireci, E.**; Gambu, T.; Sharapa, D. I.; Studt, F.; van Steen, E. Bridging Calculated Charges and Formal Oxidation State of Manganese Oxides: A DFT/DFT+U Study. *Physical Chemistry Chemical Physics* **2026**, 28 (27), 17025–17033.
7. **Sireci, E.**; Hoffman, J.-A.; Gambu, T.; Sharapa, D. I.; Studt, F.; van Steen, E. Elucidating Mn Promoter Structure and Stability on Co Nanoparticles through Machine Learning Potential-Powered Genetic Algorithm. *ACS Catalysis* **2026**.
8. Sakoglu, P.; **Sireci, E.**; Frisch, J.; Zhong, T.; van der Merwe, M.; Hoffman, J.-A.; Starr, D.; Vinogradov, N.; Jones, R.; Shavorskiy, A.; Studt, F.; van Steen, E.; Bär, M.; Jiménez, C. E. CO Pulse Enabled Time Resolved In-Situ Investigation on the Chemical Structure of Co(0001) Fischer-Tropsch Model Catalysts Under Relevant Reaction Conditions. **2026**. *In Preparation*.

D. Eidesstattliche Versicherung

Bei dieser Dissertation handelt es sich um meine eigenständig erbrachte Leistung. Ich habe nur die angegebenen Quellen und Hilfsmittel benutzt und mich keiner unzulässigen Hilfe Dritter bedient. Insbesondere habe ich wörtlich oder sinngemäß aus anderen Werken übernommene Inhalte als solche kenntlich gemacht. Ich habe die „Regeln zur Sicherung guter wissenschaftlicher Praxis am Karlsruher Institut für Technologie (KIT)“ beachtet. Die Arbeit oder Teile davon habe ich bislang nicht an einer Hochschule des In- oder Auslands als Bestandteil einer Prüfungs- oder Qualifikationsleistung vorgelegt. Die Richtigkeit der vorstehenden Erklärungen bestätige ich. Die Bedeutung der eidesstattlichen Versicherung und die strafrechtlichen Folgen einer unrichtigen oder unvollständigen eidesstattlichen Versicherung sind mir bekannt. Ich versichere an Eides statt, dass ich nach bestem Wissen die reine Wahrheit erkläre und nichts verschwiegen habe.

Karlsruhe, den 10.03.2026

Enrico Sireci