Surface ZnO\textsubscript{x} on zirconia is highly active for high temperature methanol synthesis

M.T. Nikolajsen\textsuperscript{a}, J.-C. Grivel\textsuperscript{b}, A. Gaur\textsuperscript{c}, L.P. Hansen\textsuperscript{d}, L. Baumgarten\textsuperscript{c,e}, N.C. Schjoedt\textsuperscript{d}, U. V. Mentzel\textsuperscript{d}, J.-D. Grunwaldt\textsuperscript{e,f}, J. Sehested\textsuperscript{d}, J.M. Christensen\textsuperscript{a}, M. Hoj\textsuperscript{a,\*}

\textsuperscript{a} Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby 2800, Denmark
\textsuperscript{b} Department of Energy Conversion and Storage, Technical University of Denmark (DTU), Kgs. Lyngby 2800, Denmark
\textsuperscript{c} Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe 76131, Germany
\textsuperscript{d} Topsoe A/S, Kgs. Lyngby 2800, Denmark
\textsuperscript{e} Department of Energy Conversion and Storage, Technical University of Denmark (DTU), Kgs. Lyngby 2800, Denmark
\textsuperscript{f} Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Karlsruhe 76131, Germany

Keywords:
Carbon dioxide
Methanol
Zinc
Zirconia

ABSTRACT

Zinc containing mixed metal oxides and supported zinc oxide are stable and selective methanol synthesis catalysts at temperatures where a subsequent methanol to hydrocarbons reaction can occur directly. This work provides fundamental insights into ZnO-based high temperature methanol synthesis catalysts. A pronounced support effect was observed, where ZrO\textsubscript{2} provided a beneficial effect while SiO\textsubscript{2} exerted a detrimental effect compared to bulk ZnO. Preparing co-precipitated ZnO-ZrO\textsubscript{2} catalysts showed that the initial activity correlated with the amount of amorphous ZnO on the surface of the support and that the catalytic activity increased with time on stream as zinc oxide migrated out of a solid solution with ZrO\textsubscript{2} and onto the support surface. Hence the active phase appeared to be ZnO surface species and not zinc oxide in a solid solution with ZrO\textsubscript{2}. Operando XAS coupled with modulation excitation spectroscopy unravelled that the surface ZnO was partly reduced under operating conditions, as surface ZnO\textsubscript{x}, with x approximately equal to 0.98. In-situ DRIFTS further uncovered that the surface ZnO\textsubscript{x} activated CO\textsubscript{2} and formed methanol via carbonate, formate and methoxide species. XPS finally showed that ZrO\textsubscript{2} withdrew electrons from ZnO, facilitating oxygen abstraction to form the partly reduced ZnO\textsubscript{x}, which in turn facilitated the activation of CO\textsubscript{2}.

1. Introduction

Polymeric materials play an important role in society’s permanently evolving needs and challenges because they are versatile, durable, and adaptable. From 1950 to 2019, the global production of polymeric materials increased from 2 Mt to 460 Mt, and the worldwide consumption is forecasted to be 590 Mt in 2030 [1,2]. In 2019 polyethylene, polypropylene, polystyrene, and polyethylene terephthalate accounted for 229 Mt [3]. These products are directly related to the monomers ethylene, propylene, ethenyl benzene, and para-xylene. Since these chemicals are mainly produced from crude oil, the demand for an alternative feedstock is increasing as a part of an effort to reduce global CO\textsubscript{2} emissions [4].

CO\textsubscript{2} generated from biomass or captured from the atmosphere or at a point source can be utilized to produce these monomers or monomer precursors mentioned above. A route for utilizing CO\textsubscript{2} is the combination of methanol synthesis and methanol dehydration to hydrocarbons. The methanol synthesis is equilibrium limited, but a strategy to overcome this is to combine a methanol synthesis catalyst with a zeolite methanol dehydration catalyst within one reactor [5,6]. The purpose of the zeolite is to ensure immediate conversion of the formed methanol and thereby shift the equilibrium towards the products. At the temperatures necessary for the zeolite to be active (300 to 420 °C), the traditional Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} methanol synthesis catalyst cannot be used because severe sintering of the metallic copper deactivates the catalyst [7]. Furthermore, the metallic copper causes hydrogenation of the olefins formed in the zeolite and thus disrupts the formation of unsaturated hydrocarbons [8]. For these reasons, there is currently a significant interest in finding metal oxides with high stability, high methanol synthesis activity and limited olefin hydrogenation activity.

A range of metal oxide catalysts, primarily based on ZnO, have shown high methanol synthesis activity at temperatures above 300 °C
[5,6,9–12]. Particularly catalysts combining ZnO and ZrO2 have shown an improved performance. The solid solution of ZnO-ZrO2 synthesized by Wang et al. [9] demonstrated high methanol selectivity of 86–91%, achieved with a CO2 single-pass conversion of more than 10% (at 50 bar, H2/CO2 of 3 to 4, and at 315 to 320 °C). The ZnO-ZrO2 solid solution kept its activity for 500 h on stream and was resistant to sintering at higher temperatures. Wang et al. [9] suggested that the high methanol selectivity is attributed to the synergetic effect of H2 activation on zinc sites and simultaneous activation of CO2 on the neighbouring zirconia site within a solid solution of the two components.

There has been clear evidence that the ZnO-ZrO2 combination may form a solid solution. Co-precipitating zinc oxide and zirconia produces a material where zinc is stabilizing the tetragonal phase of zirconia. Zirconia exhibits a monoclinic crystal structure at temperatures below 1170 °C, but the introduction of dopants is known to stabilize the metastable tetragonal structure [13]. Several studies have observed a systematic shift in the (101) Bragg reflection to higher 20° with increasing zinc loading until zirconia-zinc saturation ~ 33 mol% Zn [9]. Beyond this saturation, hexagonal zinc oxide starts to form and become visible in XRD [9,14–16]. The systematic shift in the (101) Bragg reflection is caused by the substitution of Zr4+ (84 Å) with Zn2+ (74 Å), which shrinks the tetragonal lattice. Similar trends have been observed with the dopants iron- and yttrium oxide with an ionic radius of 70 Å and 90 Å, shifting the (101) Bragg reflection to higher and lower 20°, respectively [17,18]. On ZnO-ZrO2 catalysts, FTIR bands around 500 and 600–700 cm−1 were associated with Zn-O-Zn and Zn-O-Zr vibrations [19] and UV–vis spectra of ZrO2 changed with Zn as dopant indicated the presence of isolated Zn2+ ions [20]. These findings have led to the belief that it is surface available Zn2+ that stabilization of tetragonal lattice, as part of a solid solution, which in synergy with Zr2+ ions [20] is the active site for CO2 hydrogenation.

By contrast, low Zn-Zn or Zn-Zr coordination numbers found by X-ray absorption spectroscopy [21] and enrichment of Zn on the zirconia surface detected by X-ray photoelectron spectroscopy [9,15] suggest that ZnO is mostly present at the zirconia surface. Even at low Zn content (Zn/Zr = 1/100), individual lattice fringes of isolated ZnO were detected by high-resolution transmission electron microscopy, indicating difficulties for Zn2+ to be present inside the ZrO2 lattice and a preference for generation of a separate ZnO phase [22]. The ZnO-ZrO2 mixed oxides thus have surface ZnO, which exists apart from the solid solution. Currently there is no clear knowledge about whether the surface ZnO or the Zn2+ within a solid solution is the primary active species.

This study aims to bridge this gap by identifying the active species in ZnO-based methanol synthesis catalysts with particular emphasis on ZnO-ZrO2 mixed oxides prepared by co-precipitation and impregnation. The purpose is to identify good candidates for the bifunctional catalytic system and clarifying the metal oxide structure–activity relation, particularly the relative importance of Zn-Zr solid solution and ZnO surface domains. ZnO was deposited on silica (SiO2), anatase titania (TiO2), monoclinic zirconia (m-ZrO2), and tetragonal zirconia (t-ZrO2) by the incipient wetness impregnation method and ZnO-ZrO2 was prepared by co-precipitation. The catalysts were characterized by X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), high-resolution scanning transmission electron microscopy (HR-STEM) and N2 adsorption/desorption (BET). Furthermore, the reaction species involved in the CO2 hydrogenation reaction on the surface of the catalyst were analysed by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The changes in the oxidation state of the supported ZnO was investigated by time resolved QEXAFS coupled with modulation excitation spectroscopy (MES).

2. Materials and method

2.1. Catalyst preparation

A series of ZnO-containing catalysts were prepared by the incipient wetness impregnation method. Firstly, the supports were dried overnight at 120 °C and the precise water uptake was determined of the dried supports. The supports were then impregnated with a solution of Zn(NO3)2·6H2O to produce catalysts with 13 mol% Zn (Zn/(M + Zn), where M is Si, Ti or Zr). Finally, the catalysts were dried overnight at 100 °C and calcined in air at 500 °C for five hours. The supports used were SiO2 255 m2/g, TiO2 161 m2/g, m-ZrO2 57.2 m2/g, t-ZrO2 145 m2/g (stabilized by Al2O3) and t-ZrO2–CeO2 105 m2/g, all provided by Saint-Gobain NorPro. Furthermore, the ZnO content on t-ZrO2 was varied from 13 to 44 mol%, all produced with the above-mentioned procedure. All impregnated samples are denoted with a forward slash as ZnO/ support. All ZrO2 supported catalysts showed HfO2 impurity, typically 1–2 mol% Hf.

For comparison, a ZnO-ZrO2 catalyst was prepared by the coprecipitation method proposed by Wang et al. [9], the hyphen is used here to denote co-precipitation. A 500 mL solution of 5.52 g Zn(NO3)2·6H2O and 37.6 g Zr(NO3)4·xH2O was added to a beaker and heated to 70 °C. A 500 mL solution of 15.3 g (NH4)2CO3 was added dropwise to the warm precursor solution under vigorous stirring. The mixture was then aged for 120 min at 70 °C, filtered and washed with demineralized water. The collected solid was dried at 100 °C overnight and calcined in air at 500 °C for five hours. Co-precipitation of a similar catalyst was repeated at a precipitation and ageing temperature of 100 °C under reflux and this sample was denoted ZnO-ZrO2-100.

Pure ZnO was prepared by precipitating Zn(NO3)2·6H2O with a Na2CO3 solution at pH = 7 and 70 °C. The precipitated ZnO was aged for 60 min at 70 °C and pH = 7, then filtered and washed with demineralized water. The solid was collected and dried overnight at 80 °C and calcined in air at 350 °C for three hours.

2.2. Catalytic activity evaluation

The methanol synthesis activity tests were conducted in a high-pressure flow reactor setup using a quartz-lined reactor tube with an inner diameter of 4 mm. Typically, 300 mg of the catalyst with a grain size of 150–300 μm was loaded into the reactor tube. Synthesis gas CO/H2/Ar with the composition of 20/60/20 vol% at 50 barg was introduced into the reactor at various temperatures in the range 280–400 °C. The reaction temperature was controlled by a N-type thermocouple placed right above the catalyst bed inside the reactor tube and an electric furnace with three heating zones. It should be noted that no pretreatment was given to the catalysts before the catalytic testing. The internal standard, argon, was used for accounting for the decrease in reaction volume. The carbon balance closed at an average of 99.95 % ± 0.99 % for all the experiments. The effluent gas was analysed by an online GC (ThermoFisher Trace 1300, assembled by Global Analyzer Solutions) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The GC column connected to the flame ionization detector was Rtx-5 (60 m, 0.32 mmID and 5 μm df), which separated the formed products (methane, methanol, and dimethyl ether). A combination of Haysep N, XL Sulfur and Molsieve SA columns were connected to the TCD detector for quantification of CO2, CO, and Ar. The CO2 conversion, oxygenate (CH3OH + CH3OCH3) selectivity, and oxygenate formation rate was calculated by Eq. (1) to (4).

\[ F_{\text{CO},\text{in}} = \frac{V_{\text{CO},\text{in}} X_{\text{CO},\text{in}} - V_{\text{in}}}{V_{\text{in}}} \]

\[ X_{\text{CO}2} = 1 - \frac{F_{\text{CO},\text{in}}}{F_{\text{CO}2,\text{in}}} \]
\[
S_{\text{CH}_3(\text{OH})+\text{CH}_3(\text{OH})} = \frac{F_{\text{CH}_3(\text{OH})\text{out}} - 2F_{\text{CH}_2(\text{OH})\text{out}}}{F_{\text{CO}_2\text{out}}} \times 100\%
\] (3)

\[
\text{Rate} = \left( \frac{F_{\text{CH}_3(\text{OH})\text{out}} - 2F_{\text{CH}_2(\text{OH})\text{out}}}{m_c} \right) M_c \text{CH}_3\text{OH}
\] (4)

Where \(V\) is the volumetric flow rate at standard conditions, \(V_m\) is the molar volume, \(m_c\) and \(y_i\) is the molar flow rate and molar fraction of component i. Both methanol and dimethyl ether can be further dehydrogenated in zeolites to form hydrocarbons. Therefore, the production of both is relevant to consider when showing the activity of the catalysts.

2.3. Catalyst characterisation

XRD analysis was conducted with a Panalytical X’Pert Pro instrument in Bragg-Brentano geometry in reflectance mode using a Cu Kα radiation source (\(\lambda = 1.541 \text{ Å}\)) at ambient conditions. The scan range was 5–70° with a step size of 0.017°. The Rietveld analysis was performed using the Topas software. To analyse the elemental composition, ICP-OES analysis was conducted on an Agilent 700 Series instrument using argon as plasmasgene. The specific surface area was analysed with the 3P instrument Sync440 and the \(N_2\) adsorption isotherm was analysed by the Brunauer-Emmett-Teller method.

The XPS measurements were performed in an ultra-high vacuum with an ESCALAB Xi+ instrument from ThermoFisher Scientific, employing a monochromatic Al Kα (1486.6 eV) X-ray source. The powdered samples were pressed onto a piece of adhesive copper tape (3 M Electrical Tape). The diameter of the analysis area was approximately 650 μm. A low energy electron flood gun was used for the neutralization of surface charge buildup. The binding energies were calibrated by using Au foil (4f\(_{7/2}\) binding energy of 83.95 eV). Etching was conducted in Ar cluster mode with an energy of 2000 eV during steps of 30 s and raster size of 3.25 x 3.25 mm\(^2\). The data were analysed with the Thermod Avantage software.

X-ray absorption spectroscopy (XAS) measurements at the Zn K absorption edge were done in transmission and fluorescence mode at the SuperXAS beamline10A, Swiss Light Source (SLS) synchrotron. QEXAFS spectra were recorded with a frequency of 1 Hz of the monochromator. Data importing and pre-processing involving energy calibration, rebinning, averaging and exporting was done using the ProQEXAFS software developed at the beamline [23]. Basic XAS data treatment of normalization, background subtraction and Fourier transformation has been conducted using Athena [24]. For the ex-situ measurements, pellets were prepared using cellulose diluted catalyst samples pressed as 13 mm diameter, self-sustaining wafers and the energy scanned in transmission mode. By taking average of 400 spectra, the k\(^3\)-weighted Fourier transformed EXAFS function (k range 3 to 12 Å\(^{-1}\)) was fitted in R – space (1 to 3 Å). The wurzite ZnO structure model (ICSD 67849) was used for fitting the amplitude reduction factor, \(S_0^2\) = 0.982, to the obtained reference spectrum of the ZnO sample. This value of amplitude reduction factor was used in the refining of coordination number (CN), interatomic distances (R), energy shift (ΔE\(_0\)), and mean square deviation of interatomic distances (σ\(^2\)) for the first and second shell of ZnO on the catalyst samples. These fits were performed using Artemis by a least-square method in the R space between 1 and 3.7 Å [24]. The surface zinc oxide did not show a Zn-Zn interaction (CN = 0), meaning that the fraction of the surface sites can be estimated from the coordination number of the second shell as proposed by Han et al. [21] in Eq. (5).

\[
\chi(\text{ZnO})_\% = \left( 1 - \frac{CN_{\text{Zn-Zn}}}{12} \right) \times 100\%
\] (5)

The coordination number of Zn-Zn in bulk ZnO is 12 and as XAS is a bulk method, the fitted coordination number is an average. The fitting results and the estimated fraction of surface ZnO\(_2\) for the catalyst samples can be found in Table S2. Linear combination fitting was conducted using the (0.13)ZnO/t-ZrO\(_2\) (no ZnO was visible from XRD and no Zn-Zn back scattering in FT-EAIXS was observed) and ZnO as references for surface ZnO\(_2\) sites and crystalline ZnO respectively and compared to the results obtained by Eq. (5). The weight percentage of surface ZnO\(_2\) sites on the zirconia supports was used for calculating the amount of ZnO\(_2\) present on the zirconia surface by Eq. (6), as XPS and XRD results suggest no to hardly any incorporation of Zn into the zirconia lattice.

\[
\%_{\text{ZnO}_2} = \frac{I_{\text{ZnO}_2}}{I_{\text{ZnO}_2} + I_{\text{ZnO}}} \times 100\%
\] (6)

Where \(I_{\text{ZnO}_2}\), \(I_{\text{ZnO}}\), and \(I_{\text{ZnO}}\) are the concentration of surface ZnO\(_2\), 0.13% of catalyst, the bulk concentration of Zn determined by ICP-OES, the weight percentage of surface ZnO\(_2\) determined by linear combination fitting and the molar mass of Zn, respectively.

For the in-situ experiments, quartz capillaries (length of 80 mm, o.d. 0.8 mm with 0.01 mm wall thickness) were loaded with 4.4 mg 100–200 μm catalyst particles diluted 1:4 in inert α-Al2O3 giving a bed length of 7 mm. To ensure a pressure tolerance of 20 bar, the loaded capillaries were glued using Araldite Rapid Epoxy to a sample holder and cured for several hours. Hereafter, the sample holder was connected to the flow setup, where a downstream mass spectrometer and 10% CO/He, CO2, 10% O2/He and He gases were connected. The capillaries were heated by radiative heaters provided by the beamline. The experimental procedure included dehydrogenation of the catalysts in O2/He with a heating ramp of 10 °C/min to 400 °C at 15 bar, followed by cooling to room temperature. Then the gas was switched to a syngas mixture (CO/CO2/ H2/He = 5/12/37/46, filtered through an active carbon filter to remove nickel carbonyls) and when a stable MS signal was achieved, the reactor was heated to 400 °C at 10 °C/min and kept at 400 °C for 2 h. Thirdly, the modulation excitation spectroscopy (MES) coupled XAS experiments were performed where the gas was switched between O2/He and syngas in intervals of 10 min at 400 °C and 15 bar. One cycle refers to the total time of O2/He and syngas exposure (10 min in O2/He and 10 min in syngas) and the switching was repeated for a total of 9 cycles. For the MES experiment, a four-way valve was used to switch the flow to the capillary between the two gas mixtures, allowing the flow of one gas mixture to the reactor and the other to a purge line. To avoid pressure fluctuations, the pressure of the purge line was adjusted by a back-pressure valve to 15 bar, keeping the reactor and the purge line pressure almost equal. Time resolved spectra were continuously recorded in transmission as well as fluorescence mode in the middle of the catalytic bed through all the above-mentioned steps. For the MES analysis, fluorescence spectra were used due to high spectral quality. The oscillation frequency of the monochromator was fixed at 1 Hz, leading to a spectrum acquisition every 500 ms. Thus, the 20 min cycle (1 period) produced around 2400 spectra, meaning a total of 21,600 spectra for 9 periods, were generated during each MES experiment. For the MES data analysis, normalized spectra were first averaged in 20 s intervals to obtain 60 time-resolved spectra for each cycle. This averaging enhanced the signal-to-noise ratio for detection of small changes during the switching [25]. The time-resolved spectra were transformed into phase-resolved spectra \(\mu(E, Δϕ)\) by using Eq. (7) [26–28]. This creates a phase-resolved set of spectra at different phase shifts \(0° \leq Δϕ < 360°\) based on the sine function of cycle time, \(T = 1200\) s. Changes occurring at identical phase shifts during each cycle were added making small changes detectable. The changes observed from the phase-resolved spectra were analyzed qualitatively and quantitatively by comparing them to the spectra of ZnO\(_2\) and (0.13)ZnO/t-ZrO\(_2\) subtracted by Zn foil.

\[
\mu(E, Δϕ) = \frac{2}{T} \int_0^T \mu(E, t) \cdot \sin \left( \frac{360°}{T} t + Δϕ \right) dt
\] (7)

Transmission electron microscopy imaging of the catalysts were per-
formed on a Thermo Fisher Spectra 200 X-CFEG (STEM) microscope equipped with Dual-X EDS detectors. The catalyst samples were crushed in a mortar and dispersed in absolute ethanol (99.9 %) before drop casting on a Cu-TEM grid covered with lacey carbon film (SPI supplies). Images and energy dispersive X-ray (EDX) spectroscopy maps were acquired in scanning transmission mode (STEM) with a probe current of 0.2 nA and a probe convergence angle of 30 mrad. Detector collection angles of 0–22 mrad and 56–200 mrad were applied for the bright-field (BF) and high-angular annular dark field (HAADF) detector, respectively. The EDX maps were acquired continuously scanning for > 10 min to obtain decent signals and were post-processed in Velox 3.8 to generate element composite images with pixel-averaged smoothing.

The reaction mechanism of CO₂ hydrogenation over (0.13)ZnO/t-ZrO₂ was probed by CO₂ adsorption, steady-state methanol synthesis, H₂ and H₂ temperature-programmed desorption/reaction with the use of in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). A Harrick high pressure Praying Mantis cell equipped with a high pressure dome and pure ZnSe windows was placed in a Vertex 70 infrared spectrometer with a liquid nitrogen cooled LN-MCT VP detector. The loaded sample was pretreated under He flow at 400 °C and 20 bar for 2 h and then cooled to the reaction temperature, where a background spectrum was acquired. For the CO₂ adsorption experiment, the gas was switched to CO₂/He where the development of peaks was continuously monitored for 60 min. Hereafter, the gas was switched to H₂/He and the change and disappearance of surface species were continuously monitored for 60 min. For the steady-state methanol synthesis experiment, after the pretreatment, the gas was switched to CO₂/H₂/He (13/38/49 vol%) and DRIFTS spectra were recorded for 60 min. After the steady-state methanol synthesis experiment, the reactor was cooled to room temperature and the gas was switched to either pure He or H₂. When a stable MS signal was achieved, the temperature was increased to 420 °C by ~ 6 °C/min.

3. Results and discussion

3.1. Support effects in ZnO catalysed CO₂ hydrogenation

Firstly, the catalytic activity as function of temperature from 280 to 400 °C was measured (Fig. S1). These temperatures are above those applied in industrial methanol synthesis, but relevant temperatures for subsequent methanol dehydration to hydrocarbons over zeolites. The results showed that at temperatures ≥ 360 °C the gas composition reached equilibrium, thus these results cannot be used for comparing the activity of the catalysts. The CO₂ hydrogenation activity results reported in the following were obtained at 320 °C, where both the reverse-water-gas-shift (RWGS) and the methanol synthesis were far from equilibrium (see calculations of approach to equilibrium in Table S1). Results with/without pre-reduction of the catalyst with hydrogen showed that the effect of this pre-treatment was negligible (see Fig. S2). Next, the effect of the feed gas composition was investigated, and it was found that the partial pressures of CO₂ and H₂ were crucial for the methanol synthesis activity over ZnO supported on zirconia. Shifting from a feed of CO/H₂ to CO₂/H₂ increased the activity dramatically (Fig. S3 and Fig. S5). Co-feeding or partially replacing CO₂ with CO did not improve the catalytic activity (Fig. S4), suggesting that the primary carbon source for methanol formation is CO₂ as also seen for Cu/ZnO/TiO₂ catalysts [29]. Increasing the H₂/CO₂ ratio also increased the rate of methanol synthesis (Fig. S5).

The oxygenate (methanol + dimethyl ether (DME)) formation rate (Eq. (3)) and selectivity (Eq.(4)) over supported zinc oxide catalysts at 320 °C are shown in Fig. 1. The results reveal a clear support effect in the ZnO catalysed methanol synthesis. Supporting zinc oxide on anatase titania or monoclinic- and tetragonal zirconia significantly increased the oxygenate formation rate compared to bulk zinc oxide. This improvement was partly due to an increase in the CO₂ conversion, but mostly due to the enhanced oxygenate selectivity, which increased from 34 % for ZnO to 68–80 % for supported zinc oxide. The DME selectivity was lower than 0.5 % on the zirconia supports, showing that these catalysts were highly selective towards methanol. Silica had a detrimental support effect on the methanol formation rate, which primarily resulted from a drop in the total CO₂ conversion compared to bulk ZnO. This silica support has previously shown a similar negative effect on the turnover frequency for the methanol synthesis over Cu/SiO₂ compared to pure Cu (i.e. Raney Cu) [29]. Infrared spectroscopy of CO on Cu/SiO₂ showed a blueshift in the C=O frequency, hence the silica exerted an electron withdrawing effect upon Cu [30], which correlated to low activity of Cu/SiO₂. It is hypothesised that similar electronic interactions between SiO₂ and ZnO might cause the loss in activity when zinc oxide is supported on silica.

As illustrated in Fig. 1, the mass-based activity and oxygenate selectivity for zinc oxide supported on titania and monoclinic zirconia showed similar results, all exerting a beneficial support effect. It was, therefore, necessary to clarify whether the beneficial supports indirectly affected an active ZnO phase on the surface or created particularly beneficial Zn²⁺ sites that are part of a solid solution with the support.

3.2. The importance of a ZnO surface phase for the catalytic activity

To elucidate the support effects, several samples with zinc oxide impregnated on tetragonal zirconia were prepared to understand the relation between zinc loading, activity and selectivity as illustrated in Fig. 2.

In Fig. 2 (a) the oxygenate formation rate was improved when increasing the Zn loading from 13 to 18 mol%, due to enhanced CO₂ conversion. Further increasing the Zn loading reduced the CO₂ conversion while maintaining the high selectivity towards methanol (Fig. 2 (b)). The major changes in catalytic properties with ZnO loading reflected changes in physical properties of the samples. The BET surface area, the amount of crystalline ZnO determined by Rietveld refinement of the XRD data, and the elemental bulk and surface composition from ICP-OES and XPS analysis are summarized in Table 1. The XRD patterns for the impregnated and co-precipitated samples are shown in Fig. 3. Fig. 3 (a) shows that with increasing zinc loading by impregnation, the tetragonal (101) Bragg reflection, observed at 2θ = 30.2°, did not shift to higher angles, which is typically observed for ZnO in ZrO₂ solid solutions [9]. This shows that the tetragonal zirconia was unaffected and that no Zn was incorporated into the lattice. Furthermore, the high surface zinc fraction determined by XPS compared to the bulk zinc fraction suggests that zinc oxide was mainly deposited on the zirconia

![Graph](https://example.com/graph.png)
The rate of oxygenate formation and CO conversion were measured for ZnO-supported on t-ZrO₂ samples (Fig. 1 and Fig. 2). The CO₂ conversion (left axis), CH₃OH and CH₃OCH₃ selectivity (right axis) against the mol% of Zn supported on tetragonal zirconia. Conditions: 320 °C, 50 barg, 15 NL/h, catalyst loading of 300 mg, feed gas composition of CO₂/H₂/Ar 20/60/20.

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET</th>
<th>Bulk Zn/(M + Zn)</th>
<th>Crystalline ZnO</th>
<th>Surface Zn/(Zr + Zn)</th>
<th>Oₓ/Oₓ⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>[m²/g]</td>
<td>[mol%]</td>
<td>[wt%]</td>
<td>[mol%]</td>
<td>[%]</td>
</tr>
<tr>
<td>ZnO</td>
<td>49.9</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>29</td>
</tr>
<tr>
<td>(0.13)ZnO/t-ZrO₂</td>
<td>118</td>
<td>13.4</td>
<td>0 (0)</td>
<td>23</td>
<td>42</td>
</tr>
<tr>
<td>(0.16)ZnO/t-ZrO₂</td>
<td>105</td>
<td>17.9</td>
<td>0.7 (0.9)</td>
<td>30 (32)</td>
<td>43 (37)</td>
</tr>
<tr>
<td>(0.29)ZnO/t-ZrO₂</td>
<td>97.4</td>
<td>29.3</td>
<td>11 (7.9)</td>
<td>32</td>
<td>49</td>
</tr>
<tr>
<td>(0.44)ZnO/t-ZrO₂</td>
<td>82.1</td>
<td>44.2</td>
<td>21 (20)</td>
<td>38</td>
<td>39</td>
</tr>
<tr>
<td>ZnO/t-ZrO₂-CeO₂</td>
<td>77.3</td>
<td>13.3</td>
<td>2.2 (2.4)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ZnO/m-ZrO₂</td>
<td>44.8</td>
<td>13.5</td>
<td>5.4 (5.1)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ZnO/TiO₂</td>
<td>103</td>
<td>13.3</td>
<td>5.3 (6.5)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ZnO/SiO₂</td>
<td>165</td>
<td>13.0</td>
<td>1 (1.1)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ZnO-ZrO₂</td>
<td>40.3</td>
<td>10.7</td>
<td>0 (0)</td>
<td>33 (31)</td>
<td>45 (30)</td>
</tr>
<tr>
<td>ZnO-ZrO₂-100</td>
<td>145</td>
<td>12.0</td>
<td>0 (0)</td>
<td>22</td>
<td>37</td>
</tr>
<tr>
<td>t-ZrO₂</td>
<td>145</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>43</td>
</tr>
</tbody>
</table>

* Determined by ICP-OES, †determined by Rietveld refinement of XRD data, ‡determined by XPS where subscript V and T denotes the oxygen vacancies (defects) and total oxygen.

Table 1 Specific surface area (BET), bulk mol%, surface Zn mol%, the weight% of crystalline hexagonal ZnO, and the amount of surface oxygen vacancies relative to the total amount of oxygen. Numbers in parentheses represent analysis of spent samples.

The conclusion that activity arises from a ZnO-type surface layer and not from Zn²⁺ ions co-solvent with ZrO₂ suggests that the ZnO surface layer dispersed on ZrO₂ was more active. This shows that crystalline ZnO was of considerable activity on its own, but also that the ZnO surface layer dispersed on ZrO₂ was higher in activity, by a factor of at least 2 according to Fig. 2 (a). For the impregnated catalysts, XRD analyses of the spent samples showed a higher crystallinity, but no shift in the (1 0 1) Bragg reflection or changes in the tetragonal unit cell volume (Fig. 3 (a-c)), which remained close to the parent t-ZrO₂ support. This shows that the Zn in the samples remained as a ZnO surface phase during the reaction and did not migrate into the support, which was consistent with their activity being unaffected by the exposure to reaction conditions (Fig. 3 (c)).

The conclusion that activity arises from a ZnO surface layer and not from Zn²⁺ ions part of a solid solution with ZrO₂ is further substantiated by the behaviour of the co-precipitated ZnO-ZrO₂ samples. For the co-precipitated ZnO-ZrO₂ samples, the tetragonal zirconia unit cell volume was significantly lower than that for the impregnated samples (Fig. 3 (c)), suggesting that Zn²⁺ ions were present in the zirconia lattice, and this uptake of dopants that stabilized the tetragonal structure at temperatures below 1170 °C [13]. TEM analysis of the ZnO-ZrO₂ sample (Fig. S15) also supported that Zn was present as a mixture of both a highly dispersed Zn phase, consistent with isolated Zn²⁺ in a solid solution, and the ~ 5 nm ZnO surface domains seen for the impregnated
samples. The co-precipitated samples thus had some zinc arranged inside the zirconia structure, as has also been observed in several other studies [9,14–16]. The ZnO-ZrO$_2$-100 sample, co-precipitated at 100 °C, had a particularly low unit cell volume (Fig. 3 (c)) and a relatively low surface ZnO content, close to the bulk composition (Table 1), which shows that this sample had a high degree of its Zn incorporated as solid solution. Two observations for the ZnO-ZrO$_2$-100 sample showed that Zn in the solid solution was not of particularly high catalytic activity. Firstly, Fig. 5 shows that ZnO-ZrO$_2$-100 had much lower initial activity than ZnO-ZrO$_2$, which had a higher surface enrichment of ZnO, although ZnO-ZrO$_2$-100 had a higher surface area. Secondly, the ZnO-ZrO$_2$-100 sample underwent a pronounced activation during the exposure to reaction conditions and after stabilization, the rate doubled compared to the initial level (Fig. 3 (c)). Analysis of the spent sample showed that this was mirrored by a downshift in the (1 0 1) Bragg reflection (Fig. 3 (b)) and a clear increase in unit cell volume (Fig. 3 (c)), which shows that the increased activity occurred when Zn segregated out of the solid solution and formed a ZnO surface layer, since crystalline ZnO was not observed.

Fig. 3 (b) shows an intensity increase in the XRD pattern for the t-ZrO$_2$ in ZnO-ZrO$_2$-100 during reaction, due to t-ZrO$_2$ becoming more crystalline and that the average crystallite size increased from about 100 to 186 Å according to Rietveld analysis, which would also result in a significant reduction of the specific surface area. Changes in the crystalline phase of the zirconia have previously resulted in an improved methanol synthesis performance [31,32]. However, the magnitude of these improvements is not comparable to the factor of > 2 in the oxygenate formation rate observed from the fresh to the spent ZnO-ZrO$_2$-100 in Fig. 3 (c). These findings are summarized in Fig. 5, showing that the two co-precipitated catalysts had similar total amount of ZnO according to ICP, but it is the catalyst with the highest amount of surface ZnO which is most active, despite its specific surface area being much lower. This shows that it is the surface ZnO and not Zn$^{2+}$ ions in a solid

![Fig. 3. (a) XRD patterns of ZnO supported on ZrO$_2$ samples, bare t-ZrO$_2$ support and ZnO. (b) Zoom in on the (1 0 1) Bragg reflection of the fresh (solid line) and spent (dotted line) impregnated ZnO-t-ZrO$_2$ (13 mol%), co-precipitated ZnO-ZrO$_2$ at 70 °C and the co-precipitated ZnO-ZrO$_2$ at 100 °C. The arrow visualizes the (1 0 1) Bragg reflection movement from fresh to spent sample. The green boxes represent ZnO placed on the ZrO$_2$ surface or in the ZrO$_2$ structure, represented as blue box. (c) The unit cell volumes calculated from the lattice parameters obtained by Rietveld refinement and the spent to fresh reaction rate ratio at 300 °C and 50 bar, after exposure for 42 h to temperatures between 300 and 400 °C at 20 °C intervals.](image-url)

![Fig. 4. (a) EDX element map of Zn and Zr of the image area in (b) high-resolution STEM image (bright field) of the (0.13)ZnO/t-ZrO$_2$ sample. The EDX quantification showed a mole fraction of Zn/(Zn + Zr) = 0.044 in this particular image area.](image-url)
3.3. Local zinc oxide environment on the zirconia surface

Due to the amorphous nature of the ZnO surface domains on the ZrO$_2$ surface, XAS was conducted to characterize and quantify these species and evaluate their relation to the catalytic activity. The Zn K-edge X-ray absorption near edge structure (XANES) and the k$^3$-weighted Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra of the as-prepared ZnO on ZrO$_2$ catalysts, Zn foil, and bulk ZnO are presented in Fig. 6(a) and (b), respectively. The XANES spectra (Fig. 6(a)) shows the absorption edge at 9662 eV for the all ZnO/ZrO$_2$ samples, the same as bulk ZnO (9662 eV) rather than metallic Zn (9659 eV) [15,21]. The absence of a signal related to metallic Zn (Zn-Zn at approximately 2.2 Å) in the FT-EXAFS spectra (Fig. 6(b)) confirmed that Zn$^{2+}$ was the only oxidation state present in all the catalysts. At low Zn loadings ≤ 18 mol%, trends associated with ZnO were observed in the shape of the XANES spectra, but no signal related to the backscattering of the next nearest neighbour Zn-Zn was visible in the FT-EXAFS spectra. This indicated that the ~ 5 nm ZnO$_2$ surface domains were a defective ZnO-phase with no repeating crystalline structure. As mentioned, the XPS evidence for surface enrichment of Zn (Table 1) revealed that these
domains were present on the ZrO\textsubscript{2} surface. As the Zn loading increased > 18 mol% for the impregnated samples, the shape of the XANES spectra resembled that of bulk, hexagonal ZnO. This confirmed that an increasing fraction of the Zn created crystalline ZnO nanoparticles, as also detected with XRD. The co-precipitated ZnO-ZrO\textsubscript{2} sample showed similar trends as the Zn impregnated samples, but with more features in the XANES spectrum (Fig. 6 (a)). The combination of XRD (Fig. 3), XPS (Table 1) and TEM (Fig. S13) suggested that this sample had most of its Zn in the form of ZnO surface domains and a minority of its Zn in solid solution, where different atomic positions may not result in regular Zn-Zr distances. Therefore, no clear Zn-Zr backscattering at distance ~3.5 Å was observed for this sample [33].

Fitting the EXAFS spectra (reported in Table S2) resulted in an interatomic distance of Zn-O ~1.98 Å and of Zn-Zn ~3.23 Å (only for Zn loadings > 18 mol%), similar to the distances observed for these two shells in pure hexagonal ZnO. Coordination numbers for the first Zn-O shell for the impregnated samples were close to 4, similar to bulk ZnO. A higher Zn-O coordination number would be expected if Zn\textsuperscript{2+} was in zigzag and into the zirconia lattice [34] or if the ZnO was hydrated. A decrease in the coordination number was seen with increasing Zn loading, which was caused by the strong correlation with the refined mean square deviation of interatomic distances (r\textsuperscript{2}). The coordination number fit of the co-precipitated ZnO-ZrO\textsubscript{2} sample was lower. However, the standard deviation did not suggest any significant difference from the impregnated samples, suggesting that most of the Zn in this sample was in the presence of ZnO surface domains.

The fractions of Zn in the disordered ZnO domains and in crystalline 3D ZnO, respectively, were estimated by Eq. (5) using the coordination number of the Zn-Zn shell and by linear combination fitting of the XANES spectra between samples having only isolated domains (here (0.13)ZnO/t-ZrO\textsubscript{2}) and bulk ZnO. Fig. 6 (c) shows the fraction of Zn in ZnO surface domains using the linear combination fitting method. Using the coordination number of the Zn-Zn shell, similar fractions of ZnO surface domains were determined. The result can be found in Table S2. With increasing Zn loading, more crystalline ZnO was formed, but a significant amount of the Zn was still present as ZnO surface domains. The amount of Zn present as ZnO surface domains was thus determined from the results in Fig. 6 (c) and the total Zn loading of the sample using Eq. (6). On this basis, Fig. 6 (d) shows the CO\textsubscript{2} conversion and CO selectivity as function of the amount of surface ZnO. This illustrates that the surface ZnO was highly selective towards methanol formation and that the amount controlled the CO\textsubscript{2} conversion. Crystalline ZnO showed methanol formation activity, but, as illustrated in Fig. 6 (d), these sites had lower selectivity towards methanol. Assuming that the ZnO domains are 2D structures with all Zn-atoms exposed and that their site density was that of the crystalline ZnO(0001) facet, the results in Fig. 6 (d) show that the turnover frequency per Zn surface atom was 17 h\textsuperscript{-1} for ZnO domains and 4 h\textsuperscript{-1} for crystalline ZnO, respectively. Other Zn-containing catalysts have been prepared for other catalytic processes, where similar surface or isolated Zn\textsuperscript{2+} sites have been concluded to be the main active site [35–38], supporting the conclusion that supported ZnO provided the active sites for methanol synthesis.

As discussed in Section 3.3 the 18 mol% Zn sample contained an appropriate amount of Zn to cover the available ZrO\textsubscript{2} surface area, and above this value 3D ZnO nanoparticles of lower activity began to occupy part of the surface. Fig. 6 (d) illustrates that this sample was also the most active as it maximized the amount of ZnO\textsubscript{2} surface sites. The results in Fig. 6 (b) and (d) thus reveal that activity of ZnO based methanol synthesis catalysts was maximized by choosing the optimal support, of which t-ZrO\textsubscript{2} was the best tested here, and loading with Zn to the maximal level at which a 2D ZnO surface layer could be maintained.

3.4. State of the ZnO surface domains and the nature of the support effect

Time resolved QEXAFS, coupled with modulation excitation spectroscopy (MES) to amplify spectral changes, was conducted to investigate the stability of the catalysts and to determine minute changes in the Zn oxidation state under methanol synthesis conditions. An initial dehydration step in O\textsubscript{2}-He did not show any changes for the Zn oxidation state, but changes in the Zn K-edge XANES when switching to syngas could suggest partial Zn reduction (Fig. S10). To amplify this effect, MES experiments with periodic switching between a syngas mixture of CO\textsubscript{2}/CO/H\textsubscript{2} (reducing gas) and an O\textsubscript{2}/He mixture (oxidizing gas), with simultaneous measurements of spectra, were conducted. To conduct the MES analysis, the changes that occur when modulating the gas phase composition must be reversible. However, irreversible formation of crystalline ZnO was observed when switching between reducing and oxidizing atmospheres for the (0.18)ZnO/t-ZrO\textsubscript{2} and ZnO-ZrO\textsubscript{2} samples, which resulted in reduced methanol synthesis activity (Fig. S11). For the (0.13)ZnO/t-ZrO\textsubscript{2} sample, the first cycle resulted in an irreversible change in the XANES spectra, which stabilized from cycles 2 to 9, as illustrated in Fig. 7 (a), which shows the averaged time resolved spectra for 9 periods. The catalytic performance was stable throughout the 9 cycles, illustrated for the first 4 cycles in Fig. 7 (b), showing stable methanol synthesis activity (MS signal at m/z = 31, due to mass overlap O\textsubscript{2} also showed intensity at this mass). The averaged time resolved intensity at 9660 eV (for cycles 2 to 9) showed clear reversible changes in the intensity going from reducing to oxidizing conditions (Fig. S12). This allowed for the phase-domain analysis.

The phase-resolved spectra as obtained from averaged time resolved spectra shown in Fig. S12 (averaging cycles 2–9) are given in Fig. 7(c) at selected phase angles. The maximum intensity of phase resolved spectra was obtained at 150°, which was used for further comparison. The decreasing intensity at 9658–9660 eV, the edge position of metallic zinc, indicated reversible changes in the Zn oxidation state. In Fig. 7 (d), the phase-resolved spectrum at 150° phase angle scaled by a factor of 50 is compared to the difference spectrum between the as prepared sample and Zn foil. This shows a reversible partial reduction of Zn under reaction conditions, where approximately 1 out of 50 Zn atoms was reduced to a state closer to metallic Zn\textsuperscript{0} than to Zn\textsuperscript{2+}. Thus, under reaction conditions, the ZnO surface species were partly reduced ZnO\textsubscript{2} species with x approximately equal to 0.98. The partially reduced ZnO\textsubscript{2} likely played an important role for the methanol synthesis activity. The thermodynamic reduction potentials of bulk ZnO to metallic Zn\textsuperscript{0} from H\textsubscript{2} (ΔG = 78.5 kJ/mol) and CO (ΔG = 63.8 kJ/mol) show that this reaction is unlikely for bulk ZnO. The MES results thus indicated that the ZnO surface phase had an increased reducibility compared to crystalline bulk ZnO.

Fig. 8 shows the Zr 3d, Zn 2p and O 1s XPS spectra for selected samples. In Fig. 8 (a), the spin–orbit doublet of the Zr 3d core level into Zr 3d\textsubscript{5/2}-Zr 3d\textsubscript{3/2} with binding energy around 182.5 and a splitting of ~ 2.5 eV, shows that the oxidation state was Zr\textsuperscript{4+} [39]. The impregnation of ZnO onto the zirconia support resulted in a shift for the Zr 3d\textsubscript{5/2} to lower binding energies, indicating a charge enrichment of the ZrO\textsubscript{2} phase. In Fig. 8 (b), a spin–orbit doublet of Zn 2p\textsubscript{3/2} and Zn 2p\textsubscript{1/2} for pure ZnO were found at 1021 and 1044 eV, which shifted to higher binding energy when ZnO was supported on zirconia. This shift suggested that Zn\textsuperscript{2+} became more electron deficient. The position of the Zn LMM Auger peaks (Fig. S13) confirmed that Zn\textsuperscript{2+} was the only oxidation state present for all the samples. In Fig. 8 (c), the O 1s peaks also shifted to lower binding energies compared to the bare t-ZrO\textsubscript{2} support, which supported that Zn\textsuperscript{2+} became more electron deficient. Lorentz peak fitting to the O 1s peak for oxygen vacancies and lattice oxygen showed no relation between surface oxygen defects and the activity of the catalyst (Table 1). However, the binding energy values for all metals showed that there was an interaction between Zn and Zr. This interaction created a more electron deficient ZnO. Withdrawal of electrons from Zn-O bonds in the surface ZnO likely correlated with the increased partial reducibility of this phase to ZnO\textsubscript{2}. This is further linked to the superior catalytic performance when ZnO was supported on ZrO\textsubscript{2}, because it was easier to abstract oxygen from a more reducible ZnO\textsubscript{2} surface and in that process oxophilic sites were created, that activated CO\textsubscript{2}. 


Fig. 7. (a) Zn K-edge XANES spectra of the (0.13)ZnO/t-ZrO\textsubscript{2} sample for cycles 1 to 9, where the gas was switched between O\textsubscript{2}/He and syngas. (b) MS signal for the first 4 cycles showing the switch between gases and the methanol formation. (c) The phase-resolved spectra obtained by Eq. (7) at different phase angles. (d) Comparison between the phase-resolved spectrum with the highest intensity (150\degree) with the difference spectrum of (0.13)ZnO/t-ZrO\textsubscript{2} minus Zn foil. Reaction conditions: 400 \degree C, 15 barg, 50 NmL/h, catalyst loading of ~ 2.5 mg (diluted 1:4 in inert α-Al\textsubscript{2}O\textsubscript{3}), feed gas composition of CO\textsubscript{2}/CO/H\textsubscript{2}/He 12/5/37/46.

Fig. 8. XPS spectra of (a) Zr 3d, (b) Zn 2p and (c) O 1 s. Solid lines represent fresh catalysts samples, ZnO and bare t-ZrO\textsubscript{2} support, while dotted lines represent spent samples.
3.5. CO$_2$ hydrogenation reaction mechanism

In-situ DRIFTS was used to study the ZnO/t-ZrO$_2$ and t-ZrO$_2$ surface reaction intermediates for methanol formation from CO$_2$ and H$_2$. In Fig. 9 (a), the CO$_2$ adsorption on the t-ZrO$_2$ support lead to observation of bicarbonate and bridging carbonate species (HCO$_3^-$, CO$_3^{2-}$ with at 1404, 1484, 1604 and 1640 cm$^{-1}$) [37,40–42]. When ZnO was added to the support, strong signals attributed to bidentate formate (HCOO$^-$ at 1360, 1382, 1595 and 2880 cm$^{-1}$) and zinc bonded carbonate (at 1508 cm$^{-1}$) adsorbates appeared [15,40,43]. The formation of formate species was still visible after H$_2$ present in the feed gas suggested that hydrogen was available at the zinc surface and that hydroxyl groups could play a role in the adsorption and activation of CO$_2$. After the CO$_2$ adsorption, the feed gas was changed to a H$_2$/He mixture and the intensity of the formate signal intensified and additional formate peaks at 2734, and 2978 cm$^{-1}$ became visible. The carbonate signals (at 1404, 1484, 1508 and 1640 cm$^{-1}$) decreased, demonstrating hydrogenation of the carbonate species into formate [44]. With t-ZrO$_2$ alone, the formate signals were observed at lower wavenumbers and the carbonate species were still visible after 60 min (Fig. S18). Thus, having ZnO on the zirconia surface provided alternative formate and carbonate binding sites and became visible. The carbonate signals (at 1404, 1484, 1508 and 1640 cm$^{-1}$) adsorbates appeared [15,40,43]. With t-ZrO$_2$ alone, the formate signals were observed at lower wavenumbers and the carbonate species were still visible after 60 min (Fig. S18). Thus, having ZnO on the zirconia surface provided alternative formate and carbonate binding sites and became visible. The carbonate signals (at 1404, 1484, 1508 and 1640 cm$^{-1}$) adsorbates appeared [15,40,43].

Fig. 9. In-situ DRIFTS measurements. (a) CO$_2$ adsorption on (0.13)ZnO/t-ZrO$_2$ and bare t-ZrO$_2$ support at 20 bar and 320 °C. (b) TPD in He and (c) TPR in H$_2$ at 20 bar after steady-state methanol formation at 320 °C and 20 bar.

Fast removal of the carbonate species by hydrogenation into formate and further into methanol occurred when switching from CO$_2$ to H$_2$ at 320 °C. As the methanol formation subsided, the intensity of the formate peaks decreased, which suggested a pathway from HCOO$^-$ to CH$_3$OH$^*$. However, formate species were still visible at the catalyst surface at low methanol concentration (Fig. S17).

The (0.13)ZnO/t-ZrO$_2$ catalyst was subjected to steady-state methanol synthesis at 320 °C and 20 bar and then cooled to room temperature. Upon cooling, methoxy species (2849 and 2952 cm$^{-1}$) became visible at the catalyst surface [15,43]. Fig. 9 (b) and (c) show the results when this cooled sample was subjected to either temperature programmed desorption (TPD) in He or temperature programmed reaction (TPR) in H$_2$. The methoxy signals quickly disappeared when the reactor was heated in He or H$_2$, and were completely removed around 140 °C. This indicated that the pathway to methanol proceeds via methoxy, but that the hydrogenation of such species was so rapid that they were only visible at low temperatures. By further heating in He the carbonate species desorbed and were removed at around 220 °C. In H$_2$ atmosphere, the removal of carbonate species occurred at 180 °C (Fig. S19). The lower temperature for carbonate removal in the presence of H$_2$ suggested that carbonate was hydrogenated to formate instead of desorbing from the surface. Around 370 °C, the formate signals disappeared showing the bonding strength order of HCOO$^-$ > CO$_3^{2-}$ > CH$_3$O$. As illustrated in Fig. S19, additional carbonate signals (at 1437 and 1573 cm$^{-1}$) became visible after formate desorption in He. These were concluded not to be relevant for the methanol synthesis activity as they are too strongly adsorbed on the surface, needing more than 410 °C to desorb. However, these signals were not observed in the H$_2$ atmosphere, suggesting that these carbonate species could be important for the methane formation.

These findings lead to the proposed reaction mechanism consisting of CO$_2$ adsorption as carbonate, hydrogenation into formate and further into methanol and finally methanol. Formate was strongly adsorbed and accumulated on the catalyst surface. Hydrogenation of formate formed short lived adsorbed methoxy, which rapidly hydrogenated and desorbed as methanol. The loosely adsorbed methoxy and the fact that carbonate hydrogénates into formate in H$_2$ atmosphere before desorption, suggested that the hydrogenation of formate into methoxy was the rate-determining step, similar to that found for the Cu/ZnO/Al$_2$O$_3$ catalyst [48].

4. Conclusions

ZnO supported on zirconia materials were highly active and selective catalysts for high temperature methanol synthesis, making them good candidates for combinations with zeolites in a bifunctional process for direct conversion of CO$_2$ into hydrocarbon products. Impregnated samples showed similar selective performance towards methanol formation as the co-precipitated samples, without any integration of Zn into the zirconia lattice as detected by XRD. Hence, a solid solution of ZnO in ZrO$_2$ was not important for the catalytic activity or selectivity. Both preparation methods resulted in catalysts where ZnO was mainly present on the zirconia surface, as determined by XPS. Furthermore, only amorphous, surface ZnO was detected by XAS at low Zn loadings. Activity measurements of two co-precipitated samples with the same bulk Zn mol%, but with a significant difference in the surface Zn concentration, demonstrated the importance of ZnO located on the zirconia surface. TEM analysis showed well-dispersed ZnO as domains of ~ 5 nm size on the zirconia surface for the co-precipitated and impregnated samples, without ZnO adopting any crystalline structure. Modulation excitation spectroscopy coupled time resolved QEXAFS showed that these Zn sites were capable of reversible, partial reduction under...
methanol synthesis conditions forming ZnO, where x was approximately 0.98. In-situ DRIFTS analysis of CO2 adsorption under methanol synthesis conditions showed a shift in the formed carbonate and formate species on the ZnO containing zirconia, compared to the bare zirconia support. Together, these findings suggested that the active phase was the partly reduced surface ZnOx, which adsorbed CO2 hydrogenated it into formate and further into methanol.

CRediT authorship contribution statement

M.T. Nikolajsen: Conceptualization, Data curation, Writing – original draft, Visualization, Investigation, Formal analysis, Methodology.

J.-C. Grivel: Writing – review & editing, Investigation, Data curation, Methodology.

A. Gaur: Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation.

L. P. Hansen: Writing – review & editing, Investigation, Data curation, Methodology.

L. Baumgarten: Writing – review & editing, Investigation, Data curation, Methodology.

N.C. Schjødt: Writing – review & editing, Supervision, Investigation, Conceptualization.

U.V. Mentzel: Writing – review & editing, Supervision, Investigation, Conceptualization.

J.-D. Grunwaldt: Writing – review & editing, Supervision, Investigation, Conceptualization.

E. Eldridge: Writing – review & editing, Supervision, Investigation, Conceptualization.


A. Urakawa, T. Bürgi, A. Baiker, Sensitivity enhancement and dynamic behavior analysis by modulation excitation spectroscopy: principle and application in


