

Structure-Dependent CO and NO Oxidation over Bimetallic PtPd/Al₂O₃ Catalysts: Impact of Pt–Pd Mixing and Alloying on Activity and Stability

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Cite This: <https://doi.org/10.1021/acs.jpcc.6c04963>



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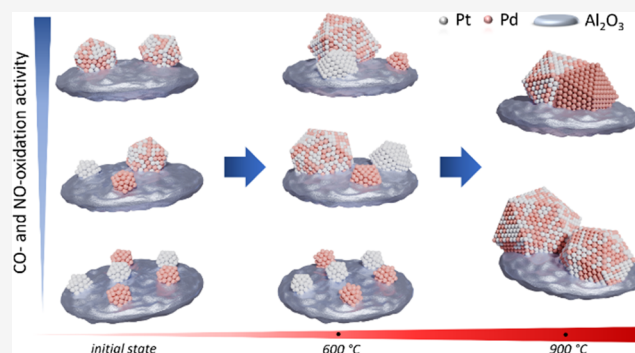
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ABSTRACT: The influence of the noble metal nanoparticle structure on the activity and stability of bimetallic PtPd/Al₂O₃ catalysts was systematically investigated. Various conventional and advanced synthesis methods were used to tune the initial Pt–Pd mixing/alloying extent. By using complementary characterization techniques, pronounced differences in the CO and NO oxidation activity could be correlated with variations in the noble metal oxidation state, particle size, and composition. The beneficial effect of Pt–Pd mixing/alloying in catalysts predominantly containing noble metal nanoparticles with a surface-averaged size smaller than ~5 nm was revealed for the CO, NO, and combined CO/NO oxidation reactions. In this regard, colloidal methods enabled the formation of homogeneously alloyed PtPd particles with a narrow size distribution and superior catalytic activity at low temperatures. However, the presence of uniform PtPd bimetallic particles did not prevent catalyst deactivation, as pronounced noble metal sintering and segregation phenomena still occurred during hydrothermal aging. In contrast, for applications operating at temperatures exceeding 600 °C, catalysts with a less uniform initial structure exhibited improved stability.



1. INTRODUCTION

Noble metals (NM) play an important role as catalyst components for numerous chemical processes such as refining, electrocatalysis, and emission control.^{1–3} Especially the removal of pollutants generated during the combustion of traditional and renewable fuels requires highly active and durable catalysts, making noble metals indispensable. Both stationary and mobile applications involve low loadings of platinum, palladium, and/or rhodium for catalyzing the abatement of CO, NO, hydrocarbons, and NH₃ emissions.^{3–5} Frequently, multicomponent systems are used to increase the performance, stability, and poisoning resistance.^{6–9} In this regard, even the earliest emission control catalyst formulations incorporated several noble metals.^{10,11} As a result, the first attempts to unravel the relationship between the structure of bimetallic catalysts and their activity were reported for Pt–Pd systems in the 1970s.^{12,13} Nevertheless, their structural dynamics and catalytic behavior remain poorly understood despite extensive research efforts.

In recent years, particularly the influence of the atomic Pt:Pd ratio on the CO, NO, HCs, and CH₄ oxidation has been investigated. While Pd-based monometallic catalysts are known to be more active for CO/HCs oxidation and Pt is more efficient for NO oxidation to NO₂, several authors reported the

beneficial effect of combining small amounts of Pd with Pt.^{9,14–16} In a mixture containing CO and various HCs, CO conversion is enhanced with increasing Pd content, and the oxidation of hydrocarbons follows that of CO, regardless of the Pt:Pd ratio.¹⁵ Ho et al.¹⁴ correlated the formation of alloyed PtPd particles with a more reduced state of Pd, which leads to an improved activity for PtPd/Al₂O₃ catalysts during low-temperature oxidation reactions. According to Hazlett et al.,¹⁷ the formation of dicarbonyl and carbonate species on Pd-rich and Pt-rich bimetallic particles is suppressed on bimetallic particles containing similar ratios of Pd and Pt during CO and C₃H₆ oxidation. The addition of Pd to a Pt/Al₂O₃ catalyst was also found to lead to a more reproducible NO oxidation performance, especially for sequentially impregnated catalysts.¹⁸ Depending on the amount of Pd in the bimetallic PtPd/Al₂O₃ catalysts, a significant enhancement of the NO

Received: July 24, 2026

Revised: September 23, 2026

Accepted: October 2, 2026

oxidation activity was also claimed by Kaneeda et al.¹⁹ In contrast, Graham et al.²⁰ found only a minor effect of Pt–Pd alloying on the NO oxidation activity of alumina-supported catalysts. Furthermore, when CeO₂ is used as a carrier material, the contribution of the noble metal–support perimeter sites remains decisive during CO oxidation.²¹

The interaction between the two metals and the evolution of the bimetallic particles has also been in the focus of several research groups. Variations in the reactive atmosphere during catalyst synthesis have been shown to induce the formation of core–shell structures. For Pt_{0.5}Pd_{0.5} nanoparticles deposited on silicon wafers, the irreversible formation of a Pd-rich shell was observed under oxidizing conditions, whereas a reduction in the Pd content of the shell was found under reductive environments.²² Li et al.²³ showed that Pt–Pd alloyed wires undergo a change in surface composition under oxidizing conditions between 400 and 800 °C, with atom probe tomography revealing a PdO layer up to 700 °C and a Pt-rich surface at higher temperatures. For bimetallic Pt–Pd catalysts, analogous restructuring trends in the bulk and surface composition were reported. Based on *ex situ* X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) characterization, Morlang et al.²⁴ observed Pt enrichment in the particle core and migration of Pd to the outer shell after hydrothermal aging at 750 °C for prealloyed particles supported on SiO₂-doped Al₂O₃. Despite surface restructuring, the addition of Pd was suggested to improve the sintering resistance of Pt/Al₂O₃ catalysts, helping to maintain reasonable NO oxidation activity even after aging at 800 °C.¹⁹ Nevertheless, Johns et al.²⁵ observed irreversible segregation of PdO as a separate phase distributed over the alumina support upon heating to 750 °C in air, while a fraction of Pt and Pd remained uniformly distributed in bimetallic particles, without forming core–shell structures. Aging at higher temperatures, i.e., 1000 °C in air, was linked by Persson et al.²⁶ to further structural modifications, including variations in PtPd particle composition and the formation of a separate PdO phase in Janus nanocomposites, consistent with analogous studies on similar PtPd bimetallic catalysts.²⁷ In a more recent investigation, Porter et al.²⁸ attributed the high activity of aged Pt–Pd-based catalysts for CO and HCs conversion, in comparison to their monometallic counterparts, to the formation of segregated biphasic PdO/PtPd Janus particles. Such particles have also previously been described to form under oxidizing conditions in CH₄ oxidation catalysts by Honkanen et al.²⁹

A common approach in earlier studies on bimetallic Pt–Pd catalysts has been the application of a pretreatment or “degreening” step to induce the formation of Pt–Pd bimetallic particles. This was necessary since the impregnation of alumina with NM precursor solutions generally yields a broad distribution of mono- and bimetallic particle compositions.^{27,29} In this regard, Martin et al.³⁰ reported that the formation of PtPd alloyed particles depends on the calcination temperature and gas atmosphere. At 500 °C, alloying is limited, and large mixed particles form only at 800 °C in dry or wet air. Simultaneously, enrichment of the surface with PdO was observed under oxidizing conditions, while both metallic Pd and Pt emerge in reducing atmospheres.³¹ Such variations in the bulk and surface composition of bimetallic PtPd particles, resulting from the specific pretreatment procedure, are expected to affect the measured activity and impair any assignment of synergistic effects. Furthermore, while the

pretreatment/degreening has the general goal of stabilizing the catalyst and obtaining a more defined structure, significant particle sintering is concurrently induced. Only recently, a more careful selection of the synthesis method was considered for increasing the Pt–Pd catalyst uniformity and ensuring more accurate structure–activity correlations. Wong et al.³² prepared SiO₂ and Al₂O₃ supported catalysts containing core–shell, alloyed, or poorly mixed PtPd particles by strong electrostatic adsorption, and investigated their activity for simultaneous CO and HCs oxidation. The authors reported the highest low-temperature activity for the sample containing core–shell Pt@Pd particles, whereas the sample containing alloyed particles performed worse than the monometallic Pt-only catalyst. In an analogous study,³³ a SiO₂-supported catalyst containing smaller and alloyed PtPd particles prepared by colloidal synthesis was found to convert CO and C₃H₆ at lower temperatures in comparison to the corresponding sample prepared by impregnation. This tendency was attributed to the more reduced state of the NMs and easier activation of oxygen. In this respect, the noble metal oxidation state was often observed to affect the oxidation activity of Pt- and Pd-based catalysts in addition to the particle size, facet orientation, and interaction with the support.^{4,34–37}

Hence, despite the high number of dedicated studies on bimetallic Pt–Pd systems, their structure and associated catalytic behavior remain intricate and difficult to decipher. Besides the often-overlooked catalyst uniformity and catalyst pretreatment, another contributing factor is that most studies assess the catalytic performance based on conversion measurements, whereas reaction rates and turnover frequencies (TOFs) are rarely considered. Yet, these descriptors are essential, as the compared catalysts frequently contain different NM particle sizes, which can strongly influence the observed activity. Finally, it is also important to consider the dynamic changes of the catalyst when studying catalytic applications that span broad temperature ranges, as structural changes can occur.³⁸

In this context, we report a systematic investigation on the influence of the synthesis route on the initial NM particle structure and on its short/long-term evolution in PtPd/Al₂O₃ catalysts for CO and NO oxidation. Several conventional and advanced synthesis methods were used to modulate the Pt–Pd interplay, ranging from weakly interacting species to intermixed PtPd nanoparticles. Next, light-off/light-out activity cycles were conducted in the low (CO oxidation up to 225 °C) and intermediate (NO and CO/NO oxidation up to 500 °C) temperature range to evaluate the effects of rapid structural alteration for prereduced and oxidized Pt–Pd bimetallic catalysts. Additionally, mild (600 °C) and harsh (900 °C) hydrothermal aging was applied to estimate the impact of more profound structural changes on activity. To interpret the CO, NO, and CO/NO activity trends, complementary *ex situ* and *in situ/operando* characterization methods were used to determine PtPd surface/bulk composition, alloying/mixing degree, particle size, and oxidation state. Overall, the results obtained underscore how the relative Pt and Pd surface fractions, nanoparticle size and structure (e.g., core–shell or uniform alloy), and NM oxidation states influence the CO/NO oxidation activity. In addition to assessing structure–activity relationships for the fresh bimetallic catalysts, this study provides insight into how the initial catalyst structure influences the state of Pd and Pt during hydrothermal aging and the resulting residual catalyst activity.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis

To obtain catalysts with distinct differences in the noble metal particle size and platinum–palladium interaction, seven different 1 wt % Pt – 1 wt % Pd/ γ -Al₂O₃ catalysts were prepared by using conventional and modern preparation techniques as described in the following:

2.1.1. Incipient Wetness Impregnation (IWI). For the preparation of the catalysts, a commercial γ -alumina support (SASOL Germany GmbH) was used after calcination at 700 °C for 5 h in static air. A first PtPd/Al₂O₃ catalyst was obtained by dropwise addition of platinum(II) bis(acetylacetonate) and palladium(II) bis(acetylacetonate) solution in acetone, yielding 1 wt % Pt and 1 wt % Pd loading. As described in detail in reference 39, the resulting sample was dried at 70 °C for 12 h and calcined for 5 h at 500 °C in static air. The sample obtained by this method will be referred to as PtPd ACAC.

A second PtPd/Al₂O₃ catalyst was obtained by incipient wetness impregnation of an aqueous solution containing tetraammineplatinum(II) nitrate (Alfa Aesar, 0.0146 mol l^{−1}) and tetraamminepalladium(II) nitrate (abcr GmbH, 0.0267 mol l^{−1}) in appropriate amounts for yielding 1 wt % Pt and 1 wt % Pd loadings. The incipient wetness impregnation step and the catalyst drying at 70 °C under vacuum were conducted on an Accelerator SLT106 Parallel Synthesizer (SLT CATIMPREG, ChemSpeed Technologies).⁴⁰ Finally, the sample was calcined in static air at 500 °C for 5 h. This catalyst sample will be referred to as PtPd TAPN.

2.1.2. Flame Spray Pyrolysis (FSP). The single flame configuration^{41,42} was utilized to prepare the PtPd catalyst. As a support precursor, aluminum acetylacetonate was dissolved in a 1:1 mixture of methanol and acetic acid. The noble metal precursors, platinum(II) and palladium(II) bis(acetylacetonate), were dissolved in toluene. The two solutions were mixed and then injected into a methane-oxygen flame (750 mL min^{−1} CH₄ and 1600 mL min^{−1} O₂) with a constant liquid flow rate of 5 mL/min. The flame led to the fast burning of the precursors and the formation of small catalyst particles with a fine dispersion of Pt and Pd, which were captured on a glass filter. The resulting powder was additionally calcined in ambient air at 500 °C for 2 h to remove any organic residues. The catalyst obtained by flame spray pyrolysis will be referred to as PtPd FSP.

2.1.3. Supercritical Fluid Reactive Deposition (SFRD). (1,5-Cyclooctadiene) dimethylplatinum(II) and palladium(II) hexafluoroacetylacetonate precursors were used to obtain bimetallic PtPd particles on the commercial γ -Al₂O₃ support. As described in detail in reference 39, the entire procedure was conducted in a stainless steel reactor ($V = 49$ cm³), and magnetic stirring was applied to the supercritical solution. Supercritical CO₂ was introduced at 353 K and 15.5 MPa for 20 h while adsorbing the dissolved precursors on the substrate. In the next step, H₂ was added to the system to reduce the metal precursors to metallic Pt and Pd, and the mixture was kept at isothermal and isobaric conditions for 2 h. Finally, the system was slowly depressurized and cooled to ambient conditions. The sample prepared by this method will be referred to as PtPd SFRD.

2.1.4. Microfluidic Synthesis (MFD). This preparation method was selected to better control the mixing of platinum and palladium in the noble metal nanoparticles. For this purpose, an in-house-designed microfluidic synthesis setup

with integrated micromixers was used, which is described in detail by Tofighi et al.⁴³ In short, a hydrogen hexahydroxyplatinate(IV) (ChemPUR) precursor was dissolved in concentrated HNO₃ under cooling in an ice bath. After complete dissolution of the Pt precursor, a solution of palladium(II) nitrate (Alfa Aesar) was added, and the resulting solution was diluted with distilled water. The final combined noble metals concentration was 7.5 mM. The reductant solution consisted of an aqueous solution of sodium borohydride (37.5 mM). Both starting solutions additionally contained polyvinylpyrrolidone (30000 wt., Sigma-Aldrich), to act as a nanoparticle stabilizer. The noble metal precursor and the reductant solutions, loaded separately in the setup, were then channeled, at equal flows (6.5 mL min^{−1}), into the microreactor channels (300 × 300 μ m²) by using pressurized N₂ (10 bar). Under these conditions, almost instantaneous mixing was achieved, and uniformly alloyed platinum–palladium nanoparticles were obtained. The resulting suspension was collected under cooling in an ice bath to stop further reactions outside the microreactor channels. To prepare the final catalyst, the nanoparticles were deposited on the commercial γ -Al₂O₃ by using a rotatory evaporator. To remove residual sodium, the sample was washed in deionized water. Next, the catalyst was dried at 70 °C for 16 h and finally calcined at 500 °C for 1 h. The resulting sample will be referred to as PtPd MFD.

2.1.5. Colloidal Synthesis Using the “Precursor” Concept. First, 0.60 mmol of palladium(II) acetylacetonate was dissolved together with 0.30 mmol of a platinum(II) acetylacetonate solution in 40 mL of oleylamine (OLAM). In the next step, the solution was purged with argon, and the reaction vessel was placed under an argon atmosphere. During this time, the mixture was quickly heated to 60 °C and then stirred at this temperature for another 30 min. Then, 2 mL (4.5 mmol) of trioctylphosphine (TOP) was added, and the mixture was heated to 200 °C while stirring. After briefly waiting, it was further heated to 300 °C, followed by an additional 30 min at this temperature under constant stirring. Finally, the mixture was cooled to room temperature, and the nanoparticles formed were precipitated with ethanol. The purification of the nanoparticles consisted of first suspending them in chloroform (CHCl₃), precipitating them again with ethanol, and separating them using a centrifuge. This process was repeated several times to ensure the purity of the particles, as described in our previous studies.⁴⁴ For the preparation of the final catalyst, the obtained PtPd nanoparticles were deposited on the commercial alumina support via wet impregnation. The resulting sample will be referred to as PtPd CD.

2.1.6. Solvent-Deficient Synthesis (SDP). Based on the method established by Smith et al.,⁴⁵ tetraammineplatinum(II) nitrate (Alfa Aesar), palladium(II) nitrate monohydrate (Alfa Aesar), aluminum nitrate nonahydrate (Alfa Aesar) precursors, and ammonium bicarbonate (Alfa Aesar) were mechanically mixed and ground in a mortar until a wet paste was formed. After about 20 min of continuous grinding, the mixture solidified. The resulting sample was calcined at 600 °C for 1 h using a heating ramp of 2 °C min^{−1}. The obtained catalyst is denoted in the following as PtPd SDP.

2.1.7. Hydrothermal Aging. Selected catalyst samples (PtPd TAPN, PtPd MFD, PtPd SDP) were aged under hydrothermal conditions by dosing a gas flow containing 20% O₂ and 10% H₂O in N₂-balance at a flow of 2.5 l·min^{−1} while

heating the catalyst bed at a ramp rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to the aging temperature. Two different temperatures, 600 and 900 $^{\circ}\text{C}$, and an aging time of 16 h were chosen to simulate mild and harsh catalyst aging conditions. After 16 h at 600 or 900 $^{\circ}\text{C}$, the samples were cooled to room temperature at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ with no changes in the gas atmosphere. Only below 200 $^{\circ}\text{C}$, the water content of the gas flow was reduced to zero to prevent condensation. After this procedure, all samples were exposed to ambient air during transfer into vials.

2.2. Catalyst Characterization

2.2.1. Specific Surface Area. After degassing the samples for 2 h at 200 $^{\circ}\text{C}$, the specific surface area of the fresh and hydrothermally aged catalysts was measured by nitrogen physisorption on a Rubotherm Belsorp mini II-unit (Bel Japan) at liquid nitrogen temperature, and the collected isotherms were interpreted using the Brunauer–Emmett–Teller (BET) method.⁴⁶

2.2.2. Elemental Analysis. The composition of all fresh samples was determined with inductively coupled plasma-optical emission spectroscopy (ICP-OES) on an Agilent 725 ICP-OES spectrometer, after dissolving the samples in aqua regia.

2.2.3. X-ray Diffraction. The X-ray diffraction patterns were acquired on a Bruker D8 Advance X-ray diffractometer with a step size of 0.016° in the 2θ range of 20 and 90° . A Cu K α X-ray source ($\lambda = 1.54\text{ \AA}$) was used.

2.2.4. Electron Microscopy. Scanning transmission electron microscopy (STEM) measurements in combination with energy-dispersive X-ray spectroscopy (EDXS) were conducted at the Laboratory for Electron Microscopy (LEM) at the Karlsruhe Institute of Technology (KIT). An FEI OSIRIS ChemiSTEM microscope operated at 200 kV or an FEI Titan³ 80–300 microscope at 300 kV acceleration tension was used in the high-angle annular dark-field (HAADF) mode. Further measurements were performed at the Institute of Nanotechnology (INT) of KIT using a Themis300 probe-corrected (S)TEM microscope and a double-corrected ThemisZ (S)TEM from Thermo Fisher Scientific. Samples were loaded on an amorphous carbon film mounted on a Cu grid by using either dry transfer or a suspension of catalyst powder in ethanol. The particle size distribution was derived using the ImageJ software by analyzing >250 nanoparticles and measuring the longest diameter of every particle detected at various magnification levels. Considering the broad distribution of the particle sizes for some of the samples, both the mean particle size and the surface-averaged particle size were calculated, as described in Boubnov et al.⁴⁷ and Ogel et al.⁴⁸

2.2.5. X-ray Absorption Spectroscopy (XAS). *Ex situ* XAS measurements were performed at the P65 beamline of DESY synchrotron, SAMBA Beamline of SOLEIL synchrotron, BM31 Beamline of ESRF synchrotron, and CatAct Beamline of KIT Light source. *Operando* XAS experiments were conducted at the SAMBA beamline using a quartz capillary reactor (ID = 1.5 mm) that was installed inside of a high-temperature oven provided by the SOLEIL synchrotron.⁴⁹ The catalysts, in the form of a sieved powder (sieve fraction 125–250 μm), were loaded into the quartz capillary reactor between two quartz wool plugs and exposed to gas mixtures containing 1000 ppm of CO, 0–1000 ppm of NO, and 10% O₂ in He. The gas flow was adjusted to obtain a similar WHSV to that applied during the laboratory tests (see below). A ramp rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ was applied between room temperature and 225 $^{\circ}\text{C}$ (CO

oxidation) or room temperature and 500 $^{\circ}\text{C}$ (CO and NO oxidation). Prior to the light-off/light-out cycles, a mild temperature-programmed reduction was conducted, heating with $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to 225 $^{\circ}\text{C}$ in 5% H₂/He. Under transient conditions, XANES spectra were collected, while EXAFS measurements were done at selected stages of the experiment. This experimental procedure was used for measurements at the Pd K-edge (24 350 eV) and at the Pt L₃-edge (11 564 eV). For selected samples, *in situ* XAS measurements were conducted under hydrothermal conditions using the edge jump capability of the BM31 beamline. XAS spectra were collected during heating up to 900 $^{\circ}\text{C}$ the catalyst bed with $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in 20% O₂, 2.5% H₂O in He-balance at a total gas flow of 50 mL min^{-1} . In this case, the samples were loaded into the high-temperature capillary cell available at BM31.⁵⁰ For all experiments, an in-house-built gas dosage system was used, consisting of an array of mass flow controllers from Bronkhorst, Swagelok piping, and a water saturator. The gas mixture was monitored at the end of the reactor with an FTIR spectrometer (MKS MultiGas 2030) and a mass spectrometer (Pfeiffer Vacuum).

The obtained *operando* XAS data sets were analyzed using the Fastosh software developed at the SAMBA beamline.⁵¹ All other *ex situ* and *in situ* data sets were evaluated using Athena and Artemis from the Demeter software package.⁵² All spectra were energy calibrated using the spectra of Pt and Pd foils measured simultaneously or before/after each experiment. Linear combination analysis was done between -15 and 20 eV around E_0 for both Pd- and Pt-edges. At the Pd K edge, a Pd-foil and a PdO-pellet were used as references, while a Pt-foil and a PtO₂-pellet were used for the LCA at the Pt L₃-edge. EXAFS data collected at room temperature prior to or after a specific catalyst treatment were evaluated in a k -space range from 3 $\text{\AA}$ to up to $14\text{ \AA}^{-1}$. The exact k -range for each specific sample and the constraints used for FT-EXAFS fits are listed in the Supporting Information. The investigated R-space ranges from 1 to 3 $\text{\AA}$, including contributions from metallic and oxidic scattering paths. FT-EXAFS fits were conducted with Pd, Pt, PdO, PtO, and PtO₂ structures obtained from the ICSD data bank, as well as modified Pt_xPd_yO approximated by PdO and PtO exchanged with individual Pd and Pt atoms. To limit the number of variables fitted to the spectra, only two different σ^2 values were used for analogous structures: σ^2 for oxidic structures and σ^2 for metallic structures.

2.2.6. X-ray Photoelectron Spectroscopy (XPS). *Ex situ* XPS was performed on mildly reduced samples (5% H₂ in N₂ at 225 $^{\circ}\text{C}$ for 30 min). XPS spectra were collected employing a monochromatic Al K α source, with a spot size of 650 μm and using a flood gun for charge compensation. All spectra were charge-referenced to the C 1s peak of adventitious carbon at 284.8 eV. Survey spectra were collected (0–1350 eV) with a pass energy of 100 eV and a step size of 1 eV, whereas detailed regions were collected with a pass energy of 25 eV and a step size of 0.05 eV. The stability of the signal throughout all measurements indicates that no structural changes were induced in the investigated catalysts. The surface compositions of the samples were determined from the high-resolution spectra, based on the sensitivity factors provided by the spectrometer manufacturer (Thermo Scientific) and available in software Advantage (v. 6.9.4). The same software was used for peak fitting; A modified Shirley background (“Smart” background) was applied to all core-level spectra prior to fitting. For each spin–orbit doublet, the splitting and area ratio

Table 1. Catalyst Structural Properties Derived Based on ICP-OES Analysis, N₂-Physisorption, XAS, and Electron Microscopy Data Evaluation^a

Sample	Pt [wt %]	Pd [wt %]	BET specific surface area [m ² /g]	Mean/surface-averaged particle size [nm]	Coordination number Pd–Pd/Pd–O–Pd (EXAFS)	Coordination number Pd–Pt/Pd–O–Pt (EXAFS)	Characteristics (STEM-EDXS/EXAFS)
PtPd ACAC	0.81	0.84	165	5.8 ± 4.8/28.2	Metallic: - Oxidic: 0.74	Metallic: 0.04 Oxidic: 0.04	<i>Pd-rich NPs</i> with low amounts of Pt and large Pt-rich core–shell particles (slightly higher Pd concentration in the shell).
PtPd TAPN	0.87	0.97	122	2.1 ± 0.7/2.9	Metallic: 0.35 Oxidic: 0.39	Metallic: 0.44 Oxidic: 0.26	<i>Monometallic Pt/Pd</i> and <i>small mixed PtPd NPs</i> .
PtPd SFRD	0.54	0.43	164	5.5 ± 1.9/7.4	Metallic: 4.51 Oxidic: -	Metallic: 1.83 Oxidic: -	<i>Monometallic Pt NPs</i> and PtPd alloyed particles with a core–shell structure. Pd content increases with the size of the particles.
PtPd FSP	0.66	0.73	236	13.7 ± 13.2/31.5	Metallic: 0.23 Oxidic: 0.19	Metallic: 1.67 Oxidic: 0.12	<i>Monometallic Pd NPs</i> and larger core–shell Pt-rich alloyed particles (>20 nm, pure Pt shell); Pt content increases with the size of the particles.
PtPd MFD	0.89	0.86	118	3.1 ± 0.8/4	Metallic: 0.87 Oxidic: 1.20	Metallic: 1.52 Oxidic: 1.25	<i>PtPd alloyed NPs</i> with narrow size distribution.
PtPd CD	0.80	0.74	163	2.7 ± 0.5/3.1	Metallic: 2.49 Oxidic: 0.01	Metallic: 3.29 Oxidic: 0.95	<i>PtPd alloyed NPs</i> with a narrow size distribution, increased Pt content in the outer shell.
PtPd SDP	0.74	0.82	290	1.1 ± 0.5/2.5	Metallic: 0.32 Oxidic: 0.43	Metallic: 0.60 Oxidic: 0.34	<i>Small and highly dispersed Pt and Pd species</i> with minimal interaction.

^aPredominant entities, due to the smaller size of the particles, are marked in italics. Further details are provided in the [Supporting Information](#) file.

were fixed to their tabulated values, and the full width at half-maximum (FWHM) was constrained to be equal between the two components.

The Gaussian–Lorentzian mixing ratio was globally fixed at 70% G/30% L. Peak positions were allowed to vary during fitting, with the exception of the Al 2p/Pt 4f region. As illustrated in [Figures S26–S28](#), for the Al 2p/Pt 4f region, the Al 2p and Pt 4f core levels overlap in the 72–76 eV binding energy range. The spectrum was fitted with an Al 2p doublet (splitting: 0.44 eV, area ratio: 2:1, FWHM_{max} of 3 eV) and Pt 4f doublet(s) (splitting: 3.30 eV, area ratio: 4:3, FWHM_{max} of 2 eV). The peak positions for the Pt 4f_{7/2} components were constrained to be below 74.9 eV (representing PtO₂). Furthermore, the Pt 4d region was used to cross-validate the Pt speciation obtained from the Al 2p/Pt 4f fit, given its lack of overlap with Al 2p.

2.3. Catalytic Activity Tests

For investigating the catalytic performance, 50 mg of catalyst powder (sieved fraction 125–250 μm) was mixed with 1000 mg quartz sand (same sieve fraction) and filled into a quartz glass reactor tube with a length of 80 cm (inner diameter 8 mm, outer diameter 10 mm). Two small plugs of quartz wool were used to fix the catalyst bed. The plug-flow reactor was mounted in a furnace so that the catalyst bed was in the middle of the furnace within a zone of homogeneous heating. The temperature was controlled and monitored using thermocouples at the beginning and end of the catalyst bed. Reaction gases were set to a weight hourly space velocity of 30000 l·h⁻¹ g_{NM}⁻¹ using Bronkhorst MFCs and then directed through the tube reactor and the catalyst bed. The gas composition was determined with an MKS MultiGas 2030 FTIR Gas Analyzer.

Before the light-off/light-out cycles, a mild prereduction step was applied in 5% H₂ in N₂ at 225 °C for 30 min with a heating rate of 10 K min⁻¹. This procedure was selected to level out the variations in the oxidation state induced by the different synthesis methods while preserving the initial size and distribution of the noble metal species. Then, CO oxidation activity was measured during two consecutive cycles between 25 and 225 °C with a gas composition of 1000 ppm of CO,

10% O₂, and an N₂ balance. Next, another reduction step identical to the first reduction step was conducted, followed by two light-off/light-out NO oxidation cycles between 25 and 500 °C in 1000 ppm of NO, 10% O₂, and N₂ as balance gas. Finally, a third reduction step, followed by a combined CO and NO oxidation test, was performed in the same temperature range, comprising two light-off/light-out cycles in 1000 ppm of NO, 1000 ppm of CO, 10% O₂, and N₂ as balance gas.

3. RESULTS AND DISCUSSION

As discussed in detail in the following, the initial catalyst structure was systematically characterized for all samples to understand its influence on the CO and NO oxidation activity of the bimetallic PtPd/γ-Al₂O₃ catalysts. Detailed investigations on the catalyst structure during activity tests and hydrothermal aging were only conducted for representative samples, aiming to uncover the effect of particle alloying/mixing on the noble metal redox response and catalyst stability.

3.1. Impact of Synthesis Method on the Initial Catalyst Structural Features

To elucidate the influence of the preparation method on the catalyst composition and properties, ICP-OES measurements were conducted in a first step for the obtained Pt–Pd/Al₂O₃ catalyst series. The results reported in [Table 1](#) indicate that similar NM concentrations around 0.8–0.9 wt % were present in all catalysts except for the PtPd SFRD and PtPd FSP samples, which contain a slightly lower NM loading. Regarding the state of the two noble metals, nearly all fresh Pt–Pd catalysts showed no characteristic XRD reflections of Pt/Pd oxides or noble metal particles ([Figure 1](#)). Only the PtPd ACAC sample exhibited reflections ascribed to metallic platinum and palladium. Additionally, the presence of γ-Al₂O₃ was confirmed in all samples, without any additional alumina phase being visible. However, an increased variation in the FWHM was noticed for the γ-Al₂O₃ XRD patterns displayed by the PtPd FSP and PtPd SDP samples, indicating a smaller crystallite size for the highly porous alumina obtained by these synthesis methods in comparison to the commercial alumina support.

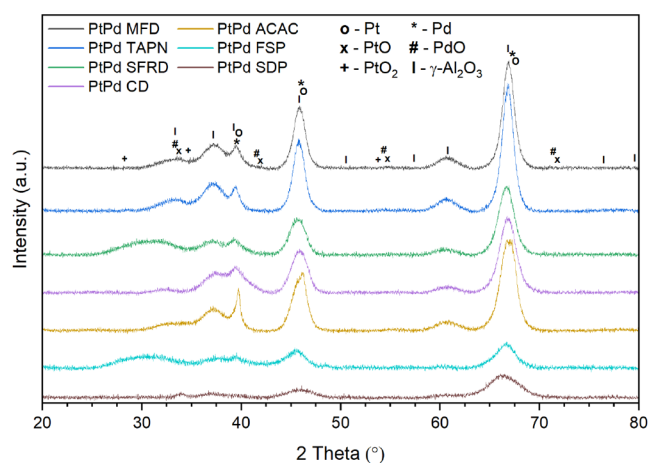


Figure 1. XRD patterns collected for the as-prepared PtPd/ γ -Al₂O₃ catalysts.

All samples were further characterized by using electron microscopy and *ex situ* XAS. According to the STEM-EDXS measurements (Figure 2d–f), the sample synthesized by impregnation with tetraammineplatinum and tetraamminepalladium nitrate precursor solutions, i.e., PtPd TAPN, contained

a narrow distribution of small (<5 nm) irregularly shaped mono- and bimetallic nanoparticles. The analysis of the corresponding XAS data indicated that most Pd species are present in the +2 oxidation state, while for Pt, the presence of partially reduced species was found based on the linear combination analysis (LCA) of the Pd K and Pt L₃ XANES regions, respectively (Figure 3a,c). The results of the Pd K edge FT-EXAFS data fitting (Figure 3b and Table S4, Figures S6 and S7) revealed the presence of Pt in the second coordination sphere as Pd–Pt and Pd–O–Pt components, representing 15% of all neighboring metal atoms (Table S31). Considering the inaccuracies, especially of the second shell fits, these values should be interpreted with caution and only used for qualitative comparison.

The catalyst obtained by incipient wetness impregnation with the platinum and palladium acetylacetonate precursors, i.e., PtPd ACAC, contained a broad range of nanoparticle sizes (Figure S1e,f). A significant contribution of relatively small PtPd particles (between 1 and 5 nm) with a Pd-rich surface and bulk composition (Pd₉Pt₁ according to EDXS line scan analysis, see Figure S1f) was found, accompanied by larger core–shell particles (>20 nm, mean size 30.7 nm) with a Pt-rich surface (Pd_{2.5}Pt_{7.5} shell) and bulk (almost pure Pt) composition. The analysis of the *ex situ* XANES data (Figure S4) revealed an average Pd-oxidation state of ~+2. Analogous

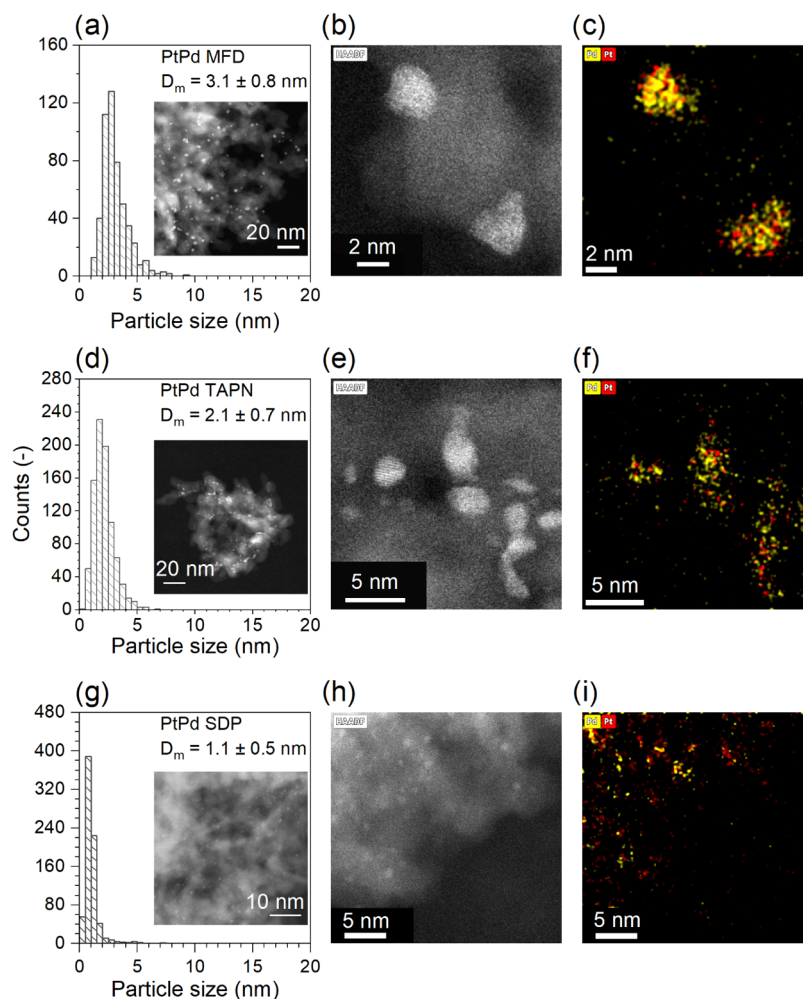


Figure 2. Particle size distributions, representative HAADF-STEM images, and EDXS maps of PtPd MFD (a–c), PtPd TAPN (d–f), and PtPd SDP (g–i) catalysts.

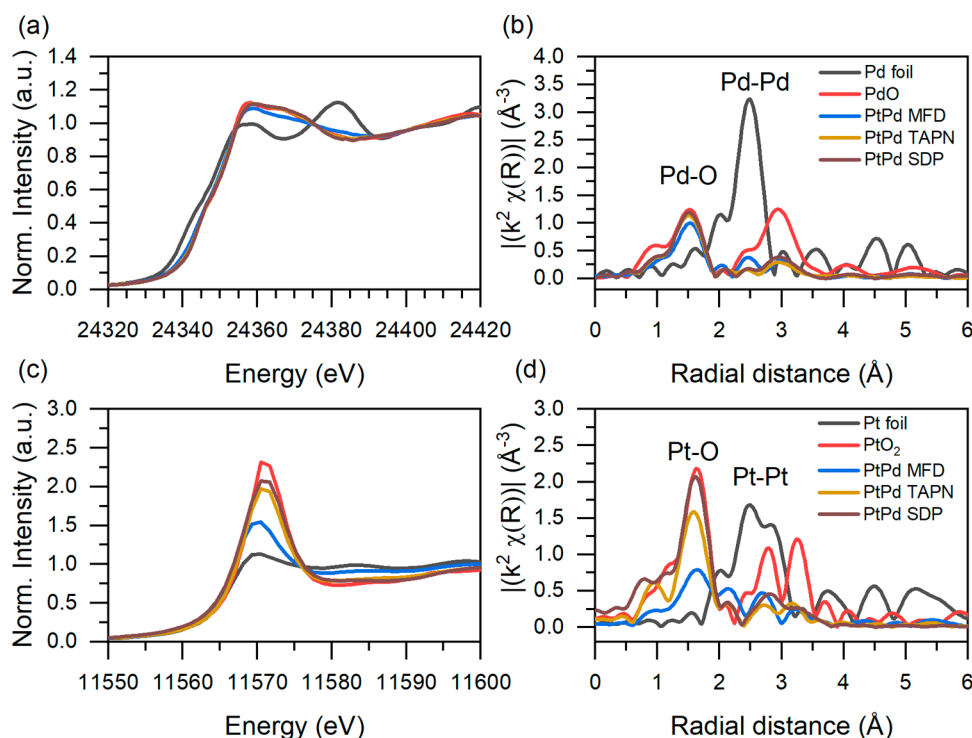


Figure 3. *Ex situ* XANES spectra collected at Pd K edge (a) and Pt L₃ edge (c) and the corresponding k^3 weighted FT-EXAFS spectra (b, d) for the fresh PtPd MFD, PtPd TAPN, and PtPd SDP catalysts.

to the PtPd TAPN sample, a high average oxidation state was derived for Pt in the as-prepared PtPd ACAC sample by LCA ($\sim +2.43$). In line with the electron microscopy data, the results of the FT-EXAFS fitting (Table 1, Tables S7 and S23) indicated only minimal mixing between Pt and Pd with a Pd–Pt/Pd–O–Pt neighbor ratio of just around 2% (Table S31).

The sample obtained by flame spray pyrolysis, i.e., PtPd FSP, displayed a broad bimodal distribution of noble metal particle sizes (Figures S1c and S2). Small Pd-rich (almost pure Pd) nanoparticles with a mean size of ~ 2.9 nm were found alongside large core–shell particles (mean size ~ 32 nm) with a Pt-rich surface (2–4 nm shell of almost pure Pt₁₀₀) and core with a composition close to Pd₁Pt₉ based on STEM-EDX line scans (Figure S1d). The LCA of the XANES data collected at the Pd K and Pt L₃ edges revealed an average oxidation state of +1.74 for Pd and +1.23 for Pt (Figure S4a and b). The analysis of the FT-EXAFS data uncovered an important metallic Pd–Pt contribution, leading to a mixing ratio of Pt neighbors for every Pd atom of 40% (Tables 1 and S31).

A broad but unimodal size distribution was identified for the PtPd SFRD catalyst (Figure S1a) obtained by supercritical fluid reactive deposition, with most particles between 1 and 10 nm. However, when the particle composition is looked at, a bimodal distribution is observed. Particle composition varies in two distinct regions: 1–5 nm and >5 nm size ranges. The first category corresponds to Pt-rich nanoparticles (almost pure Pt, according to the EDXS analysis). The bulk concentration of Pd increases with particle size, reaching over 80 atom % for sizes between 7 and 12 nm (Figure S1b). Nevertheless, an almost equimolar alloyed PtPd shell with a thickness of 1–2 nm surrounds the Pd-rich core of larger particles. Based on the analysis of the XAS data (Figure S4), an average Pd-oxidation state of +0.6 was found for this sample, while the Pt oxidation state was +0.63. For both noble metals, this partially reduced

oxidation state reflects the reduction step applied during catalyst synthesis. FT-EXAFS data fitting (Table S8) showed that for nearly all Pd atoms, around 26% of the metal neighbors in the bimetallic particles are represented by Pt atoms, confirming the strong dominance of alloyed PtPd particles (Table S31).

The two samples produced by colloidal methods (PtPd MFD and PtPd CD) contained exclusively small homogeneous (67% Pd and 33% Pt) nanoparticles with an average size of 2.7 nm for PtPd CD (Figure S1g and h, Figure S3a) and 3.1 nm for PtPd MFD (Figure 2a–c). The analysis of the XANES and EXAFS spectra helped visualize the differences between them. The noble metal species in PtPd CD were mostly reduced with an average oxidation state of +0.68 for Pd and of +0.31 for Pt (results of LCA of the XANES spectra shown in Figures 3 and S4). The fitting of the FT-EXAFS data confirmed the high interaction between Pd and Pt with a Pd–Pt neighbor ratio of 55% in PtPd CD (Table S31). In the PtPd MFD sample, the average oxidation state was +1.57 for Pd and +1.14 for Pt, revealing a considerably more oxidized structure, i.e., a PtPdO_x phase. In this case, the fitting of the FT-EXAFS data shown in Figure 3b confirmed the contribution of both Pd–Pt and Pd–O–Pt paths, and an overall Pd–Pt neighbor-share of 37% (Table S31).

Finally, the PtPd SDP catalyst prepared by mechanical solvent-deficient precipitation exhibited a homogeneous distribution of small noble metal clusters and subnanometer particles with an average size of 1.1 nm, as shown in Figure 2g–i. The small size of the particles present in this sample did not allow a conclusive assessment on how well Pt and Pd species are mixed due to the limited spatial resolution of the EDXS analysis (Figure S3b). However, the LCA of the XANES spectra indicates the formation of PtO₂-like entities with an average Pt oxidation state of +3.35, while Pd is present as PdO-

Table 2. Surface Composition of the Mildly Prereduced Catalysts, Considering Platinum, Palladium, Aluminum, and Oxygen, as Indicated by the Results of XPS Analysis

Species	FSP	MFD	SDP	SFRD	TAPN	ACAC	CD
	atom %	atom %	atom %	atom %	atom %	atom %	atom %
Al	32.2	32.8	36.5	38.2	38.7	38.4	31.0
O	64.4	62.8	63.4	61.82	61.0	61.2	61.2
Na	-	3.2	-	-	-	-	-
P	-	-	-	-	-	-	1.63
Pt	1.0	0.5	0.04	0.02	0.12	0.26	0.31
Pd	2.4	0.7	0.09	0.04	0.14	0.13	0.93
Pd/Pt atomic ratio	2.34	1.4	2.25	2	1.17	0.5	3
Pd/Pt theoretical atomic ratio ^a	2.03	1.77	2.03	1.46	2.05	1.9	1.7

^aValues calculated based on the ICP-OES measurements reported in Table 1.

like species with an oxidation state of +1.98, which suggests poor intermixing.^{25,53} Accordingly, the fitting of the FT-EXAFS data (Tables S5 and S21) indicates a limited interaction between the two noble metals, with only 19% of Pd-neighboring metal atoms being Pt (Table S31). This result, combined with the high average oxidation state of Pt, could be explained by the different crystal systems of PdO (tetragonal) and PtO₂ (orthorhombic) phases, which prevented the formation of homogeneous PtPdO_x mixed oxides.

All samples were further characterized by XPS measurements following a mild reductive treatment at 225 °C for 30 min in 5% H₂. During the sample transfer, samples were exposed to air, which may have slightly altered the oxidation state of the outer surface layers of the noble metal particles. Nevertheless, significant changes in the bulk properties are not expected at ambient temperature. This step was also applied prior to the first light-off/light-out activity cycle in order to level out the oxidation state of the metal species without significantly altering the NM particle size or bulk structure. For the same reason, XPS was selected as a surface-sensitive characterization method to minimize the risk of inducing structural modifications during analysis, which may occur when other surface-sensitive methods are applied (i.e., chemisorption measurements involving sample prereduction at higher temperatures). Consistent with the electron microscopy investigations, distinct differences were identified in the surface composition of the bimetallic PtPd catalysts (Table 2). The excess Pd in catalyst compositions is reflected by the Pd:Pt atom % ratios in most samples. Higher concentrations of Pd were found on the catalyst surface compared to the bulk catalyst composition (Table 1) for PtPd CD, PtPd SFRD, PtPd FSP, and PtPd SDP catalysts. In contrast, the derived Pd:Pt atomic ratios were lower for PtPd MFD, PtPd TAPN, and particularly for PtPd ACAC, in comparison to those expected based on the noble metal loadings. These discrepancies suggest a notable difference between the surface and core compositions of the noble metal particles across all samples. According to the XPS data, Pt and Pd are present in most samples in a partially reduced state (Table S35). This trend is caused by the relatively low temperature of the prereduction step as well as the subsequent exposure of the catalyst to ambient atmosphere, confirming the mild character of the catalyst pretreatment. Nevertheless, under reaction conditions, the reoxidation of the NMs is to some extent hindered by the presence of CO in the gas mixture.^{34,54} Additionally, due to the selected synthesis protocols, significant Na and P traces were identified for the PtPd MFD and PtPd CD catalysts, respectively.

All in all, based on the electron microscopy investigations, five categories of samples were identified among the as-prepared catalysts containing (i) high number of small Pd-rich NPs and large Pt-rich particles, i.e., PtPd ACAC, PtPd FSP; (ii) high number of small Pt-rich NPs and large Pd-rich core-shell particles with an alloyed shell, i.e., PtPd SFRD, (iii) containing small alloyed/mixed PtPd NPs, i.e., PtPd MFD and PtPd CD, (iv) containing small bimetallic but also monometallic particles, i.e., PtPd TAPN, and (v) containing highly dispersed Pd and Pt species, i.e., PtPd SDP. In addition, two groups of samples with either a narrow or broad particle size distribution could be established: the PtPd MFD, PtPd CD, PtPd TAPN, and PtPd SDP catalysts exclusively contain noble metal nanoparticles, which are distributed within the 1–7 nm range. In contrast, all other samples showed a broadening of the size distribution beyond 10 nm. Finally, the catalyst surface composition determined by XPS measurements suggests distinct differences, depending on the synthesis method. Hence, all of these variations underline the necessity to use complementary characterization methods for capturing robust structure–activity correlations.

3.2. Investigations of the Catalytic Behavior during CO, NO, and CO/NO Oxidation

In general, variations in the bulk composition of PtPd particles are known to affect catalyst evolution during operation.^{25,28,55} At the same time, the number and nature of surface sites represent the ruling factors for the catalytic activity. These characteristics are influenced by the nanoparticle size and shape, which affect the interactions with CO and NO. A size between 2 and 3 nm was found to be optimal for Pt NPs during CO oxidation, whereas larger particles of approximately 3–4 nm are necessary to achieve high NO oxidation activity.^{39,47,48} This behavior is also linked to the corresponding oxidation states of the noble metal. The metallic state of Pt was found to promote the low-temperature activity for both reactions.^{35,48} Similarly, Pd-based catalysts show enhanced activity after reductive treatment.^{36,37} In contrast, PdO-containing samples display poor NO oxidation activity.³ Incorporating Pd into Pt-based catalysts is proposed to enhance CO oxidation¹⁵ and ensure higher stability during NO oxidation. However, its effect on NO conversion remains debated.^{3,19,24}

Considering these factors, several parameters were examined in this study during the evaluation of the CO, NO, and CO/NO activity trends: (1) catalyst surface composition, (2) alloying/mixing degree – bulk composition – of PtPd particles, (3) particle size, and (4) average oxidation state of

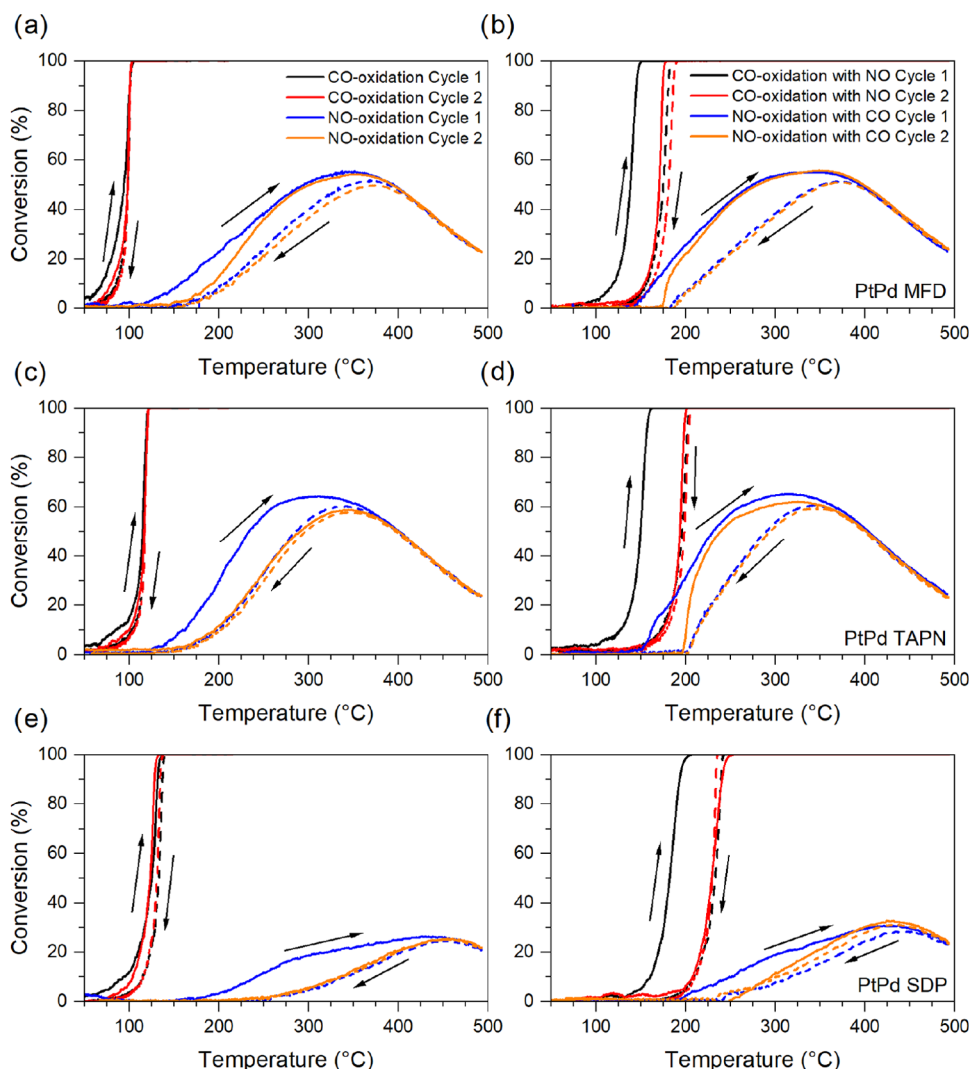


Figure 4. Catalytic activity for CO-only and NO-only oxidation (left) and combined CO/NO oxidation (right) for samples PtPd MFD (a, b), PtPd TAPN (c, d), and PtPd SDP (e, f). Light-off curves are shown in solid lines and light-out curves in dotted lines.

the metal species. Complementary characterization data sets and methods were used to derive and validate trends in catalyst performance, thereby mitigating the statistical limitations associated with each technique. As previously described, the size distribution and the bulk composition of the as-prepared samples were determined based on detailed electron microscopy and XAS investigations (Table 1), whereas the catalyst surface composition was evaluated by XPS measurements (Tables 2 and S35) and EDXS line scans of noble metal particles. With respect to the oxidation state of the two noble metals, the catalyst series synthesized in this study was investigated in the prereduced state as well as after one catalytic cycle, corresponding to an oxidized/partially oxidized state. Herein, only a mild prereduction treatment in 5% H_2 in N_2 was applied at 225 °C for 30 min. While substantial structural changes were previously reported to occur for bimetallic particles at higher temperatures, Pd migration on the surface in oxidative or reducing atmospheres is rather limited under 500 °C.^{22,23} Moreover, for very small noble metal nanoparticles/clusters (≤ 1 nm), van den Oetelaar et al.⁵⁶ found that such segregation phenomena are suppressed due to the low number of bulk Pd atoms. Accordingly, our experimental protocol, basically mild in conditions, is expected

to avoid pronounced structural changes in the bimetallic PtPd particles, such as surface enrichment or sintering. At the same time, it ensures to some extent a comparable catalyst state independent of the synthesis method, only influenced by structure-dependent trends.

Two light-off/light-out cycles were carried out for each gas composition, i.e., for CO, NO, and CO/NO oxidation. As demonstrated in the following, the first activity cycle resembled the prereduced state of the catalyst, while the second light-off/light-out cycle reflected the activity of oxidized/partially oxidized Pt and Pd species. The obtained activity data are depicted in Figure 4 for the samples PtPd MFD (Figure 4a and b), PtPd TAPN (Figure 4c and d), and PtPd SDP (Figure 4e and f), corresponding respectively to three categories of catalysts containing: (i) only alloyed/mixed oxide PtPd particles, (ii) a mixture of mono- and bimetallic PtPd particles, and (iii) highly dispersed Pt and Pd entities with limited interaction. The results obtained for the other PtPd samples investigated in this series are reported in Figures 5, 6, and S9 in the Supporting Information. For comparison, activity data is shown in Figure S10 for the corresponding monometallic Pt/ Al_2O_3 and Pd/ Al_2O_3 catalysts.

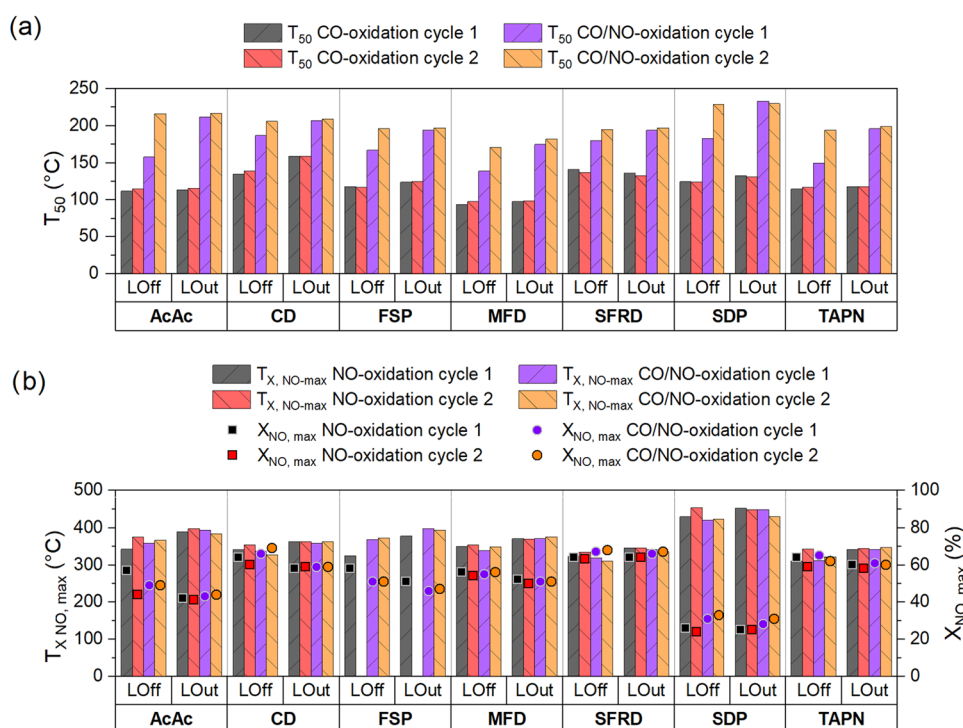


Figure 5. (a) Temperatures of 50% CO conversion as bar graphs for CO-only and CO/NO oxidation; (b) temperatures of the NO conversion maximum as bar graphs and maximum NO conversion as dots. Measurements were conducted after a prereducive step at 225 °C during the two consecutive light-off/light-out cycles of CO-only, NO-only (1st cycle in black, 2nd cycle in red), and CO/NO oxidation (1st cycle in purple, 2nd cycle in orange) for the differently synthesized catalysts. Gas mixture: 0–1000 ppm of CO, 0–1000 ppm of NO, and 10% O₂ in N₂.

3.2.1. Activity of the Prerduced Catalyst State.

Overall, the effect of catalyst prerduction was mostly visible during NO oxidation and combined CO/NO oxidation. During the first CO oxidation light-off, the influence of the prereducive step was noticed only at temperatures below T_{50} (the temperature corresponding to 50% CO conversion). Despite the same nominal catalyst composition, a clear difference in the catalytic performance was observed by comparing the CO-only oxidation activity of the prerduced samples in Figures 4, 5, and S10. For the monometallic samples, a slightly lower T_{50} was measured for the Pd/Al₂O₃ (106 °C) sample in comparison with Pt/Al₂O₃ (126 °C). Additionally, the Pt/Al₂O₃ catalyst also showed a typical hysteresis profile between the light-off/light-out curves (Figure S11). When comparing the bimetallic catalysts, close intermixing of Pt and Pd in alloyed or mixed oxide particles appeared beneficial for CO conversion. The lowest light-off temperature of 95 °C (Figures 5 and S13) was measured for the prerduced PtPd MFD sample, whereas the PtPd SFRD catalyst required a temperature approximately 45 °C higher to achieve the same CO conversion during the first light-off. Considering the variations in the composition of the bimetallic particles (Table 1), the positive effect of PtPd mixing on the catalytic activity that is dominant in the PtPd MFD catalyst aligns well with previous literature studies.^{33,57} While a positive effect of residual sodium present on the catalyst surface (see Table 2) cannot be excluded, the negative effect on activity through poisoning has been as well reported in literature during CO and NO oxidation combined with a preferential location of sodium and other alkaline/alkaline earth metals on the catalyst support.^{58,59} The contrasting result obtained for the PtPd SFRD catalyst, despite its high Pt concentration on the surface, is consistent with the presence of large Pd-rich

particles combined with a lower noble metal loading in this sample (Table 1 and Figure S1). Relatively low CO oxidation activity was displayed by the PtPd CD and PtPd SDP samples. For the catalyst prepared by colloidal synthesis using the ‘precursor’ concept (T_{50} = 135 °C), the lower CO conversion, which was observed despite high PtPd mixing, may be attributed to the presence of phosphorus traces (Table 2) originating from the use of trioctylphosphine as capping ligand that is known to adversely affect CO oxidation performance.⁶⁰ At the same time, the poor activity of the PtPd SDP sample can be associated with the small size of Pt and Pd entities, which is known to be detrimental for catalytic oxidation.^{39,45} In contrast, all samples containing a high number of small Pd-rich NPs, i.e., PtPd FSP, PtPd ACAC, and PtPd TAPN catalysts, converted CO at intermediate temperatures, i.e., in the range 110–130 °C. With respect to the light-off and light-out conversion loop, almost no difference was noticed between the T_{50} temperatures of the heating and cooling steps for all samples (Figure 5), with only a minor hysteresis or inverse hysteresis tendency. This behavior could be explained by the broad particle size distribution in most samples and by their different interaction with CO,³⁹ as well as by the simultaneous presence of Pt and Pd monometallic nanoparticles, which are known to typically exhibit conventional or inverse hysteresis profiles during CO oxidation, respectively.^{61,62}

As previously mentioned, after catalyst prerduction, a significant increase in NO conversion was measured for most samples (Figures 4, 5, S10, and S14). When considering the highest conversion achieved, the degree of PtPd intermixing does not appear to have a major impact on the NO conversion. The highest NO conversion at low temperature was displayed by the PtPd TAPN catalyst (63% at 308 °C), which contains relatively small bimetallic but also monometallic particles. This

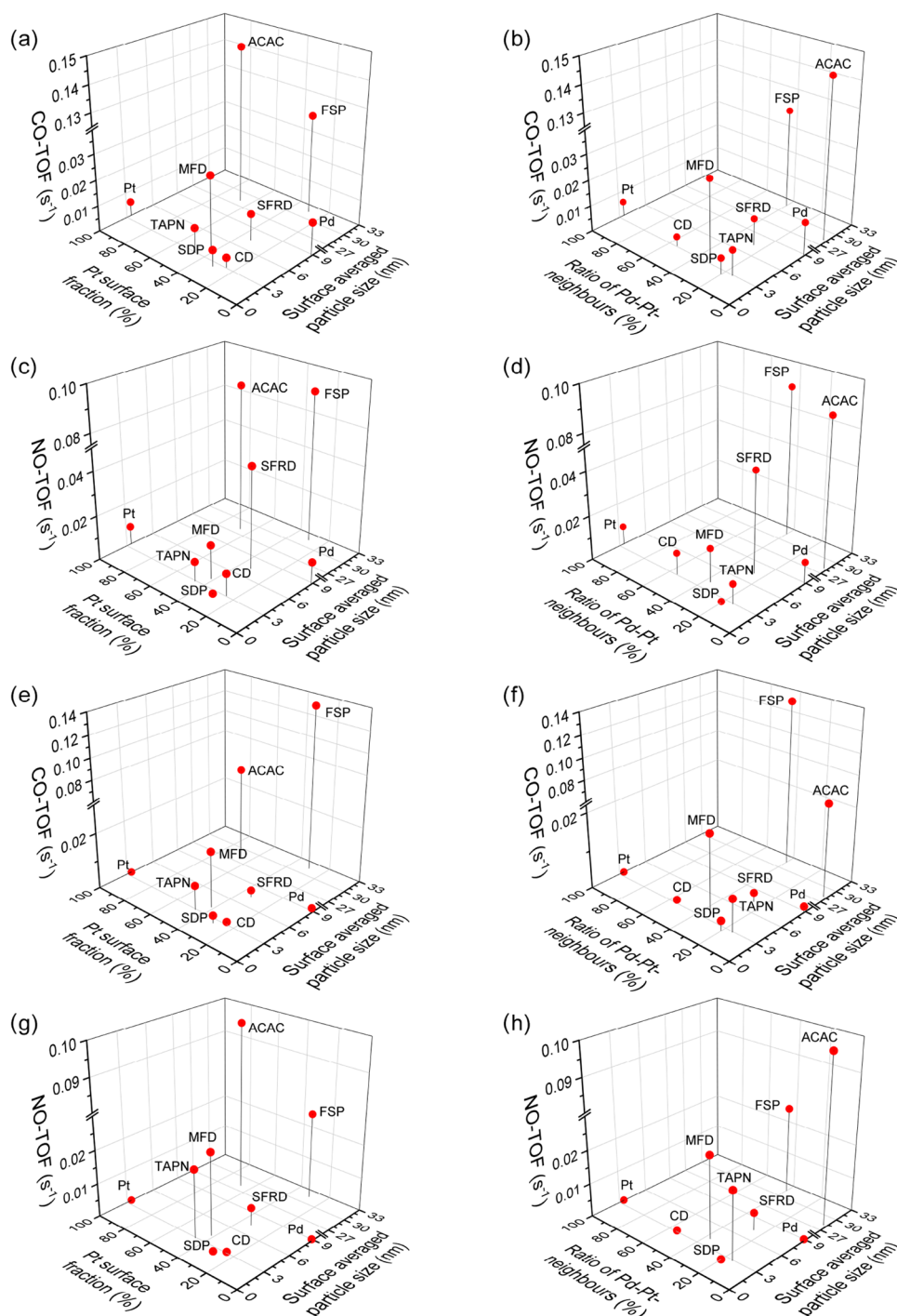


Figure 6. Apparent TOFs calculated for CO conversion at 75 °C (a, b) and NO conversion at 150 °C (c, d), as well as for CO conversion in the presence of NO at 120 °C (e, f) and NO conversion in the presence of CO at 170 °C (g, h) during the first light-off measurements. TOFs are plotted against the catalyst Pt surface concentration (atom % obtained from XPS investigations) and NM surface-averaged particle size (a, c, e, g), and against the ratio of Pd–Pt neighbors (%) obtained from fitting of EXAFS data) and NM particle size (b, d, f, h).

sample also contains a high Pt concentration on the surface compared to the Pd atom %. This is closely followed by the PtPd SFRD (64% at 325 °C) and PtPd FSP (58% at 325 °C) samples, comprising Pt-rich particles larger than 2 nm.⁴⁸ Only at slightly higher temperatures, the catalysts obtained by colloidal methods exhibited similar activities (between 55 and 65% NO conversion at 335–345 °C) as the PtPd ACAC sample (58% at 339 °C). Analogous to the CO oxidation activity, the lowest NO conversion was measured for the PtPd

SDP catalyst (~24% at 453 °C), which contains highly dispersed subnanometer species.

For the combined CO and NO oxidation, a clear shift of the CO conversion toward higher temperatures was observed over all investigated catalysts (Figures 4 and S10). A variation in the measured T_{50} values between 50 and 120 °C was noticed during CO conversion when NO was present in the gas mixture. This effect was assigned in the literature to the competition for the active sites and inhibition by NO_x of CO

conversion.⁶³ The CO conversion followed a similar trend as observed during the CO-only oxidation light-off: PtPd MFD > PtPd TAPN > PtPd ACAC > PtPd FSP > PtPd SFRD > PtPd CD > PtPd SDP. Also in this case, the well-mixed PtPd particles in the PtPd MFD catalyst showed the highest CO oxidation activity, whereas the catalysts containing small Pt-rich nanoparticles or highly dispersed species with limited interaction exhibited low CO conversion. The oxidation of NO in the presence of CO over the prerduced PtPd/Al₂O₃ catalysts showed only a slightly different trend compared to NO-only oxidation. The PtPd TAPN and PtPd SFRD samples still displayed the best NO conversion performance (65 and 67% conversion at ~312 and 319 °C, respectively), closely followed by the PtPd CD catalyst (71% at 325 °C). At a temperature approximately 25 °C higher, the PtPd MFD catalyst achieved 55% NO oxidation to NO₂ while the PtPd ACAC sample reached ~50% conversion. A similar NO oxidation activity was measured over the PtPd FSP sample around 360 °C. Finally, the PtPd SDP sample converted only 25% NO despite the high reaction temperature (452 °C).

To establish a clearer correlation between the observed activity trends and the composition of the PtPd particles in each bimetallic sample – particularly linking the performance to the number and nature of surface sites – TOF values were calculated for the three different reaction conditions. As described in detail in the following, several assumptions were made for the TOF calculations. In particular, it was assumed that all noble metal surface atoms act as active sites, which means that the reported values should be interpreted as apparent or averaged TOFs. All apparent TOF values were calculated based on the actual catalyst loading measured by ICP-OES. Considering the broad particle size distribution obtained for the PtPd FSP and PtPd ACAC catalysts, the surface-averaged particle size was used for the calculation of the TOFs. Based on the results of the XPS investigations, an estimation of the share of Pt and Pd species on the catalyst surface could be made. The calculated TOFs for CO-only and NO-only conversion at 75 and 150 °C, respectively, as well as those calculated at 120 and 170 °C during CO/NO oxidation, are plotted in Figure 6. TOFs are plotted against the surface-averaged NM particle size (electron microscopy data in Table 1) and the average Pt surface fraction (XPS data in Table 2). To visualize the impact of the bulk structure, the same TOF values were additionally displayed against the ratio of Pt neighbors of every Pd atom in the bimetallic particles, as derived from the FT-EXAFS analysis. Finally, the TOFs were plotted against the Pt surface concentration derived based on the STEM-EDXS area/line scans of bimetallic particles (Figure S17). In this way, not only a relation between the catalyst activity and surface/bulk structure of the bimetallic particles can be derived but the outcome can also be validated by complementary characterization methods. Nonetheless, due to relatively poor signal-to-noise ratio of the XAS measurements, complex composition of PtPd particles and simplified fitting model, especially the trends derived by utilizing the FT-EXAFS fitting results, should be interpreted with caution and in combination with the complementary characterization data provided in this study.

For the CO-only oxidation reaction, a clear difference was noticed between the samples comprising a bimodal size distribution and those containing a narrow size distribution. Thus, the highest TOF was obtained for the PtPd ACAC catalyst, which contains a significant share of large Pt-rich

particles with a very low mixing/alloying degree (Figure 6a and b, Table S31). However, a good Pt–Pd mixing was identified on the surface of the noble metal particles by electron microscopy (Figure S1). This sample is closely followed by the PtPd FSP catalyst, which also contains large Pt-rich particles but with significant mixing/alloying extent according to the EXAFS data evaluation. Among the samples with a narrow particle size distribution under approximately 5 nm, the highest TOF during CO-only oxidation was determined for the catalyst comprising bimetallic PtPd particles with a mean particle size of ~3.1 nm and almost equimolar Pd:Pt distribution on the surface, i.e., the PtPd MFD sample. This TOF value is significantly higher in comparison to those calculated for the monometallic Pt- or Pd-based samples. Furthermore, all other bimetallic catalysts containing particles with a surface-averaged size smaller than ~5 nm with an uneven composition or poorly interacting Pt and Pd entities exhibited lower TOFs. A comparable TOF to that measured for the monometallic Pd-based catalyst was shown by the PtPd TAPN sample, which mainly contains monometallic Pt/Pd and small mixed PtPd NPs. Similarly, the PtPd SFRD sample displayed a higher TOF value relative to the monometallic Pt-based sample. In contrast, a lower TOF was calculated over highly dispersed NM entities as present in the PtPd SDP catalyst. Also, the PtPd CD sample showed a low TOF value during CO-only oxidation, similar to that exhibited by the Pt-only monometallic sample. As previously mentioned, the presence of phosphorus traces (Table 2) is most likely responsible for the inhibition of the low-temperature activity of this sample, although the NM particle size and composition may still play a role.

A similar trend regarding the calculated TOFs and the benefit of having larger and at least partially alloyed PtPd particles was observed during CO oxidation in the presence of NO (Figure 6e). The beneficial effect of a large noble metal particle size is also reflected by the high TOFs exhibited by the PtPd ACAC and PtPd FSP samples during NO-only and combined NO/CO oxidation (Figure 6c,g). This tendency is consistent with that reported for monometallic Pt-based catalysts by previous studies.⁴⁷ A high TOF value was also calculated for the PtPd SFRD sample during NO-only oxidation, which as well contains a high number of Pt-rich particles in addition to a few Pd-rich particles in the 2–6 nm range (Figure S1). Among the other samples identified by the XPS measurements to contain notable amounts of both noble metals on the catalyst surface, the PtPd MFD catalyst exhibited the highest TOF during NO-only oxidation (Figure 6c). Moreover, upon CO addition to the gas mixture, the synergistic behavior of the two noble metals became even more pronounced: the PtPd MFD sample, comprising uniformly mixed PtPd particles and a close to equimolar share of the two noble metals on the surface, displayed the highest TOF for both CO and NO oxidation compared with the other samples containing mono- and/or bimetallic NM particles in the 2–5 nm size range. Also, when the TOFs were plotted against the bulk composition of NM particles (Figure 6f and 6h) or surface composition derived from the STEM-EDXS analysis (Figure S17), a good to moderate degree of Pt–Pd alloying/intermixing appeared to be beneficial for NO oxidation in the presence of CO.

3.2.2. Activity of the Oxidized/Partially Oxidized Catalyst State. At temperatures corresponding to complete CO conversion, the catalyst bed is almost entirely exposed to

oxidative conditions.³⁵ This leads to a gradual oxidation of the noble metal species from the surface toward the bulk, a process directly affected by the noble metal particle size.³⁴ Consequently, the catalyst is expected to evolve from a reduced state at the beginning of the first light-off to partial or completely oxidized noble metal species during the following activity cycles, depending on the temperature range. However, in the presence of CO, the reduction of the noble metal species can occur during light-out, especially if a low ramp rate is applied.⁶⁴ During our experiments, the ability of CO to regenerate the metallic state of the two noble metals is reflected in the very similar T_{50} temperatures measured during the second cycle of CO-only oxidation (Figures 5 and S10 and S12). Hence, also in this case, the highest activity at low temperature was displayed by the PtPd MFD sample, containing small alloyed PtPd nanoparticles (mean size of 3.1 nm). Notably, for an oxidized/partially oxidized catalyst surface, the beneficial role of a PtPd mixed/alloyed state is also displayed by the highest TOF value calculated for this sample (Figures S15 and S16). Slightly lower TOFs were obtained for the PtPd ACAC and FSP catalysts containing large noble metal nanoparticles. These are followed by the PtPd SFRD sample comprising a high number of Pt-rich nanoparticles in the 2–6 nm range and alloyed surface for larger particles (Figure S1). At the opposite side is the PtPd SDP sample, which showed a TOF lower than that calculated for the monometallic Pt/Al₂O₃ catalyst. Nonetheless, when comparing the corresponding apparent activation energies during the second cycle of CO-only oxidation (Table S34), the lowest values were obtained for the PtPd TAPN (41 kJ/mol), PtPd FSP (44 kJ/mol), and PtPd ACAC (48 kJ/mol) catalysts, whereas the highest was shown by the PtPd SFRD sample (109 kJ/mol). At the same time, a slightly lower apparent activation energy was obtained for the PtPd MFD catalyst (62 kJ/mol) in comparison to the monometallic counterparts (81 kJ/mol for Pt and 70 kJ/mol for Pd). This discrepancy in the trends of the apparent activation energy indicates that additional kinetic factors must be considered when interpreting catalytic performance such as CO binding strength and alloying effects.

In contrast to the CO oxidation conditions, in a NO-only oxidation gas mixture, the noble metal species are expected to undergo a more pronounced bulk oxidation due to the broader temperature range of the light-off/light-out cycle, with an oxidation extent also depending on the noble metal particle size. This situation is confirmed by the clear decrease in the NO oxidation activity for all samples investigated, already during the light-out of the first NO oxidation cycle (Figures 4 and S10). After this stage, no further variation in the catalytic performance was recorded during subsequent activity cycles, as shown by the overlap of the two light-out curves for all samples. This response of the catalytic system is confirmed by virtually the same activity measured for selected samples without prereduction steps between the CO, NO, and CO/NO oxidation cycles (Figure S12 and Table S33). The highest NO conversion during the second light-off was exhibited by the PtPd SFRD sample: 63% of NO was converted at 339 °C. This behavior could be explained by the significant share of Pt surface sites and only slightly larger size of Pt-rich particles (Tables 1, 2, and Figure S1), which are known to promote NO oxidation.⁴⁷ This was followed closely by the PtPd TAPN, CD, MFD, and FSP samples. The PtPd SDP catalyst maintained the lowest activity measured already during the first light-off/light-out cycle. When comparing the TOFs, the very good

performance of the PtPd SFRD sample was mirrored by the highest TOF value calculated for this catalyst (Figures S15 and S16). Significantly lower TOFs were determined for the other catalysts. Nevertheless, the alloyed state of PtPd particles seems to be advantageous during NO oxidation, especially for noble metal nanoparticles smaller than ~5 nm. Overall, all samples comprising a high Pt surface concentration or containing alloyed PtPd nanoparticles convert NO more efficiently than monometallic Pt and Pd catalysts. Nevertheless, although the differences are less pronounced than during CO oxidation, the apparent activation energies determined for NO oxidation do not follow this tendency for all catalysts. In this case, the lowest values were obtained for the PtPd SDP and PtPd FSP catalysts, despite their substantially different NO oxidation activity. This indicates that other structural factors influence the observed catalytic performance.

Analogous to the NO-only oxidation measurements, a lower overall activity was measured during the second light-off of NO and CO oxidation in comparison to the activity of the prereduced samples. However, whereas the NO oxidation was mostly affected around the reaction onset temperature, a pronounced shift toward higher temperatures was observed for CO conversion over all investigated samples. Only the PtPd SDP catalyst showed a slight decrease in the T_{50} temperature during CO oxidation (Figure 5). In this case, a mild sintering or restructuring of the small and dispersed NM species during the first light-off/light-out cycle could explain this tendency. The lowest T_{50} temperature for CO conversion was measured for the PtPd MFD sample. When comparing the TOFs, the presence of large noble metal particles seems to be the main controlling factor for CO oxidation in the presence of NO. Nevertheless, the beneficial effect of mixing/alloying in PtPd nanoparticles is still visible if the catalysts contain small noble metal particles. Analogous to the NO-only oxidation, the highest activity and TOF during NO oxidation in CO presence was obtained for the PtPd SFRD catalyst, which contains larger noble metal particles (mean size/surface-averaged size: 5.5/7.4 nm) with a Pt-rich or alloyed surface. A high TOF was once again measured for the PtPd MFD sample among the catalysts containing NM particles with a surface-averaged size smaller than ~5 nm.

To assess the influence of the initial catalyst state on the Pt and Pd evolution during short light-off/light-out cycles and long-term aging, three representative catalysts were selected for further investigations: PtPd MFD, PtPd TAPN, and PtPd SDP. These samples represent three different states of PtPd interaction, as revealed by the electron microscopy investigations (Figure 2) and EXAFS analysis, and also according to the synthesis methods: homogeneous mixed/alloyed nanoparticles (PtPd MFD), intermixed/alloyed and monometallic nanoparticles (PtPd TAPN), and mostly monometallic and highly dispersed species with minimal interaction (PtPd SDP). Moreover, these samples contain relatively small nanoparticles with narrow size distributions.

3.3. Catalyst Structural Changes during Short Light-Off/Light-Out Cycles

To elucidate the influence of the initial NM mixed/alloyed state on the catalyst evolution under reaction conditions, *operando* XAS measurements were conducted for the PtPd MFD catalyst at the Pt L₃ and Pd K edges during CO and CO/NO oxidation. Additionally, the final state of the noble metal particles after the reaction procedure described in the previous

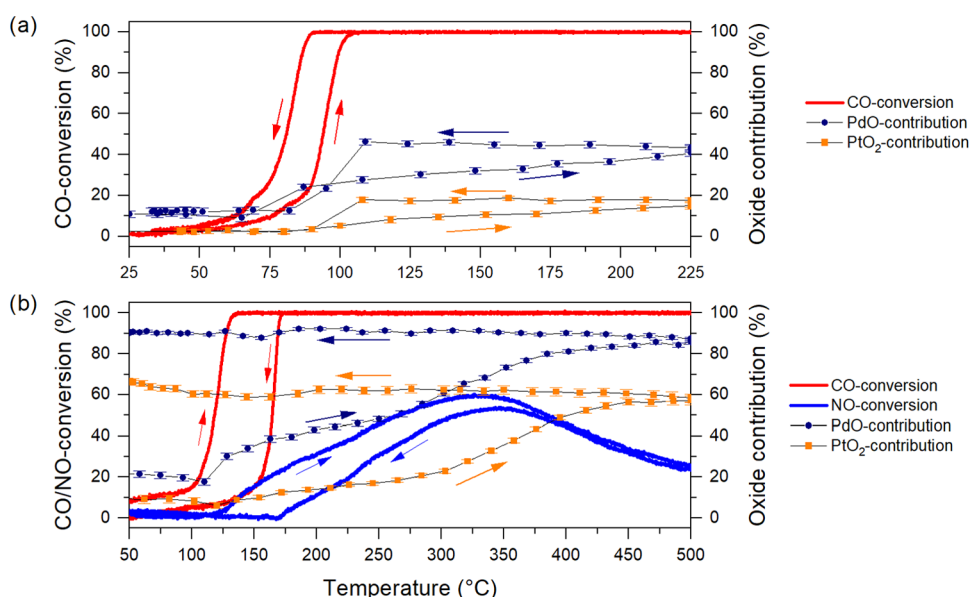


Figure 7. Results of LCA of the *operando* XANES spectra measured at the Pt L₃ and Pd K edges of the PtPd MFD catalyst during (a) CO oxidation in 1000 ppm of CO, 10% O₂/He, and (b) combined CO/NO oxidation in 1000 ppm of CO, 1000 ppm of NO, and 10% O₂/He (b).

chapter was verified by HAADF-STEM and EDXS investigations. To prevent interferences due to the presence of other monometallic or irregularly mixed species, only this sample was selected for detailed investigations into the noble metal redox response and structural changes in bimetallic particles. Figure 7 shows the results of the linear combination analysis (LCA) of the XANES data after catalyst prereduction during the CO-only and CO/NO oxidation cycles. For the LCA, metallic Pt/Pd foils were used as reduced reference states and PdO/PtO₂ as references for the oxidized states.

Starting with a predominantly metallic state for both Pt and Pd species after the mild prereduction treatment, a change of the oxidation state was observed during the CO oxidation light-off to 225 °C for both NMs (Figure 7a). In both cases, the oxidation of the noble metal species occurred only after the complete conversion of CO was achieved. According to previous studies,³⁵ as the temperature increases and CO is converted, the reaction zone shrinks toward the beginning of the catalyst bed, leading to the exposure of the rest of the catalyst bed to oxygen. Consequently, the noble metal species are progressively oxidized, which was also observed in this study. However, for the PtPd MFD catalyst, only about 40% of the Pd species and ~15% of the Pt sites were in oxidized state at 225 °C. This low oxidation extent of both noble metals is probably triggered by the combined effects of a slightly larger size for the bimetallic particles (Table 1), the narrow temperature range of the catalytic test, and the close intermixing of Pt and Pd. During the reaction light-out, the typical hysteresis loop is better visible in the capillary reactor used for the *operando* XAS investigations. This behavior can be explained by the use of an undiluted catalyst bed, which enables improved heat transfer during the exothermic CO conversion.³⁹ The electronic state of both noble metals remains relatively stable under these conditions until the temperature reaches the CO oxidation extinction point. Below ~75 °C and at about 30% CO conversion, both Pt and Pd are rapidly reduced back to their metallic state.

In contrast, during the CO/NO oxidation cycle, a significantly stronger increase in the oxidation state was

observed for both noble metals as soon as the complete CO conversion was achieved (Figure 7b). Moreover, in line with the NO₂ formation, the oxidation rate increases when reaching maximum NO conversion and drops again afterward. Due to the higher temperatures applied during this experiment, combined with the NO₂ presence, about 90% of Pd and 60% of Pt species were in an oxidized state at 500 °C. The difference recorded between the two noble metals during the relatively fast heating step could be caused by the higher surface concentration (Table 2) and superior thermodynamic stability of PdO in comparison to PtO₂.²³ At the same time, this state could be due to the preferential formation of a Pd_xPt_yO-mixed oxide structure, with Pt in a partially reduced state. This tendency is supported by the identical charge and tetragonal crystal system of PdO and PtO phases, which are prerequisites for good intermixing in bimetallic particles. This latter assumption is especially valid for the PtPd MFD catalyst, as this sample contained highly interacting and well-mixed/alloyed PtPd nanoparticles in the as-prepared and reduced state. Depending on the PtO₂ phase (α —hexagonal, β —orthorhombic or β' —tetragonal),⁶⁵ the formation of significant amounts of Pt⁴⁺ would lead to phase segregation because of the different crystal structures, which would limit the intermixing with PdO.

An even more pronounced discrepancy in comparison to the CO-only oxidation cycle was noticed during the light-out of the combined CO and NO oxidation cycle. Only a minor fraction of Pd species appears to be reduced after CO is no longer completely converted during the light-out step. For Pt, a similar behavior could be observed, and 65% of the Pt species remain oxidized at the end of the test. This behavior is clearly caused by the presence of NO in the gas mixture, which most probably adsorbs on the catalyst surface as nitrates and nitrites,¹⁸ hindering the complete noble metal reduction. Additionally, the good intermixing of Pt and Pd seems to diminish the overall redox response of both noble metals during light-off and light-out of CO and combined CO and NO oxidation in comparison to the corresponding monometallic catalysts.^{47,48} The higher oxidation state of the noble

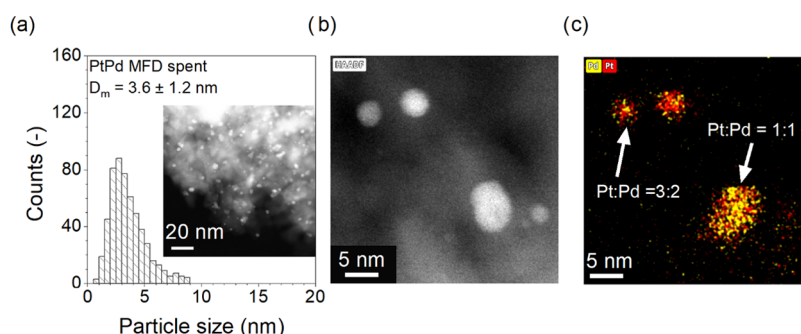


Figure 8. Particle size distribution (a), HAADF-STEM (b) image, and EDXS map (c) of the PtPd MFD catalyst after CO-only, NO-only, and combined CO/NO oxidation reaction (2 cycles to 225 °C and 4 cycles to 500 °C, respectively).

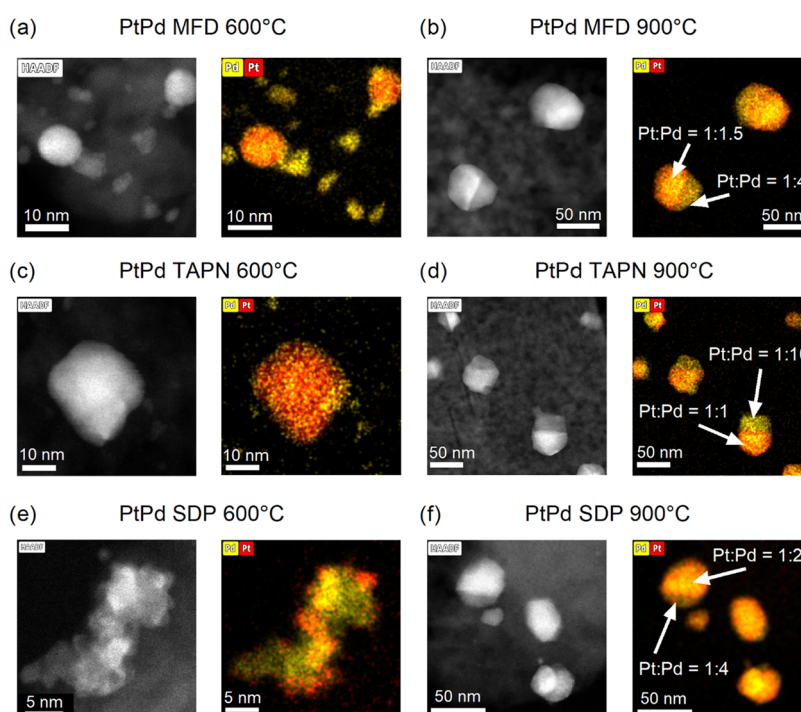


Figure 9. HAADF-STEM images and EDXS mapping of PtPd MFD (a, b), PtPd TAPN (c, d), and PtPd SDP (e, f) catalysts aged at 600 °C (left) and 900 °C (right).

metals, which leads to lattice expansion at the end of the catalytic cycles to 225 °C/500 °C, was confirmed by electron microscopy measurements on the spent PtPd MFD catalyst. Representative HAADF-STEM images, EDXS maps, and particle size distributions are shown in Figures 8 and S19, indicating a slightly larger mean size of PtPd nanoparticles (3.1 nm for the as-prepared catalyst versus 3.6 nm for the spent catalyst). Nevertheless, while broadening of the size distribution was observed, no pronounced segregation effects of the nanoparticles could be observed in the corresponding EDXS maps.

3.4. Impact of Hydrothermal Aging Conditions on Catalyst Structure and Performance

After deriving structure–activity correlations for the fresh Pt–Pd/ γ -Al₂O₃ catalysts, three representative samples were selected to assess the influence of the initial catalyst structure on the hydrothermal aging behavior and residual activity of the bimetallic catalysts. All belong to the category of catalysts with a surface-averaged particle size smaller than 5 nm, which is important for monitoring particle sintering. Additionally, these

catalysts contain well-mixed PtPd particles (PtPd MFD) or poorly interacting Pd and Pt species (PtPd SDP) or a mixture of monometallic and bimetallic particles obtained by conventional impregnation (PtPd TAPN). To evaluate the effect of a longer exposure time at elevated temperatures on the bimetallic particles structure as well as on the related CO and NO oxidation activity, the PtPd MFD, PtPd TAPN, and PtPd SDP catalysts were hydrothermally aged for 16 h at 600 and 900 °C. According to previous literature, the two selected temperatures should represent the margins for the auto-oxidation of platinum and palladium oxides, respectively.^{66,67} Around these temperatures, the most pronounced structural changes are expected to occur due to the differences in the crystal lattice structure of the metallic and oxidic phases. Besides changes in crystal structure, the mobility of various species can also change, leading to different particle growth mechanisms. 600 °C can easily be reached in exhaust systems during high engine load, making this set point a relevant reference condition. On the other hand, 900 °C represents rather extreme conditions, e.g., regeneration of the diesel

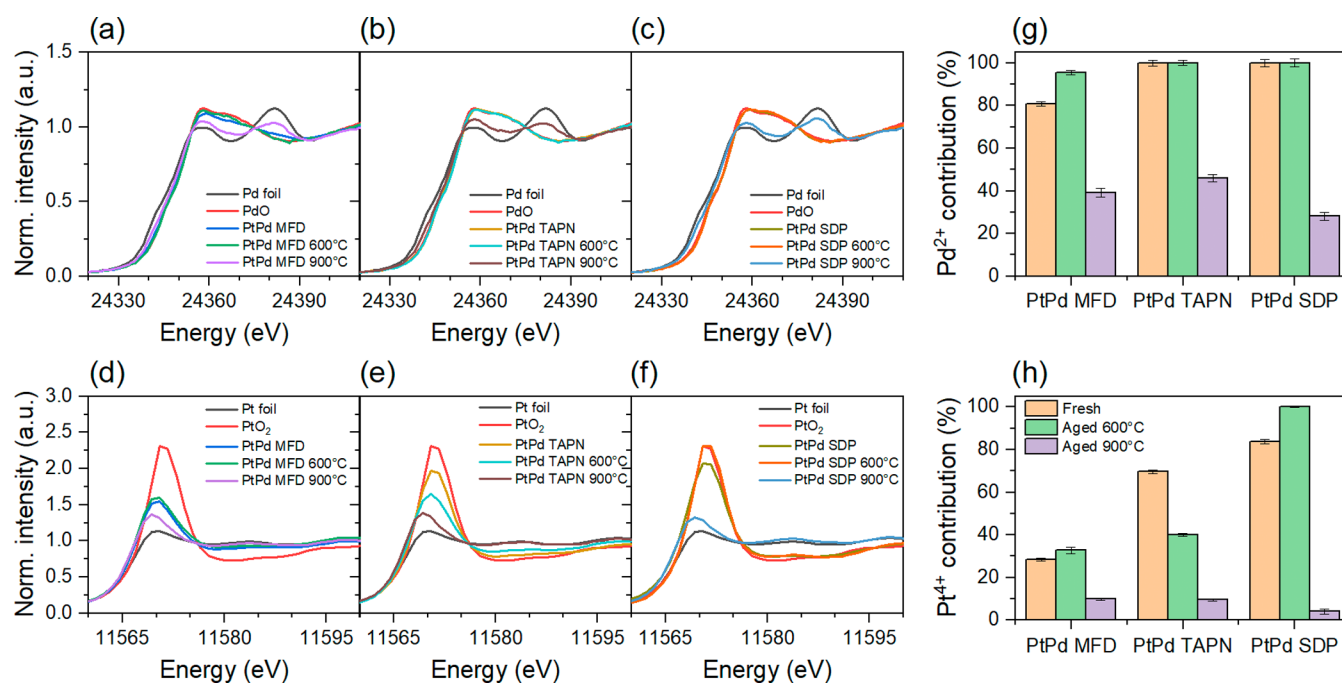


Figure 10. *Ex situ* XANES spectra for the aged PtPd/Al₂O₃ samples at Pd K edge (a–c) and Pt L₃ edge (d–f). The results of the LCA of the XANES region are depicted on the right for Pd (g) and Pt (h) speciation.

particulate filter, but it is applied in this study to mimic accelerated aging under oxidizing conditions or catalyst degradation under reducing gas atmosphere.

The resulting aged samples were analyzed by HAADF-STEM combined with EDXS mapping. Additionally, *ex situ/in situ* XAS measurements were conducted to reveal structural and electronic changes in the noble metal nanoparticles. As shown in Figures 9 and S23, all three PtPd/Al₂O₃ samples showed significant variations in particle size and structure after both aging procedures. After 16 h of hydrothermal aging at 600 °C, a clear segregation of the bimetallic particles into large Pt-rich nanoparticles and small Pd-rich/PdO-like nanoparticles was observed for the PtPd MFD and PtPd TAPN catalysts. The two samples exhibited a mean particle size of 6.3 nm (initial 3.1 nm) and 8.2 nm (initial 2.1 nm), respectively. Based on these values, it appears that the higher degree of Pt–Pd interaction in the MFD sample has a certain effect on preventing strong sintering during aging. In this regard, the larger and less mobile particles present in the fresh MFD sample in comparison to the TAPN catalyst are known to contribute to the higher catalyst stability, as previously observed for monometallic samples.⁴⁸ On the other hand, the structural change with the highest impact remains the segregation process with the formation of larger Pt-rich NPs due to the autoreduction and coinciding increased surface mobility of Pt, as has been reported previously for monometallic Pt/Al₂O₃ catalysts.⁶⁸ At the same time, smaller Pd-rich nanoparticles are observed in this sample. This process was confirmed by the profile of the *ex situ* XANES spectra recorded for the aged catalysts, as seen in Figure 10g and h and Figure S5. Whereas Pd mostly remained oxidized in the MFD sample (95% Pd²⁺ species according to the LCA results), Pt was in a more reduced state (~70%). In the case of the PtPd TAPN catalyst, the formation of small oxidized Pd-rich and large metallic Pt-rich particles after aging at 600 °C was even more visible in comparison to the fresh catalyst state.

Nevertheless, small Pt-rich nanoparticles remain present in this sample (Figure S21), pointing out the effect of the particle size on the reducibility of platinum species.

The fitting of the FT-EXAFS data collected at the Pd K edge confirmed these observations (Tables S10, S12, and S15, Figures S6 and S7). The segregation of PtPd particles was particularly visible for the PtPd MFD catalyst. This sample showed a lower contribution of the Pd–Pt and Pd–O–Pt paths in the Pd K edge FT-EXAFS spectrum after sample aging at 600 °C (Table S32). At the same time, the share of the Pd–O–Pd path is dominant, which is in line with the diminished presence of Pt atoms in the Pd-rich phase (Table S10). After aging under identical conditions, the PtPd TAPN sample exhibited a high Pd–O–Pd contribution as well, confirming the segregation effect (Table S12). However, due to the lower mixing extent of Pt and Pd phases in the as-prepared catalyst, no clear variation was noticed in the calculated mixing ratio upon sample aging at 600 °C (Table S32). A similar behavior was identified for the PtPd SDP sample. The analysis of the corresponding FT-EXAFS data collected at the Pt L₃ edge (Figures S8 and S9) appears to be in line with these findings. The Pt–Pt path is dominant in PtPd MFD (Table S24) and PtPd TAPN (Table S28) catalysts upon aging at 600 °C, but the Pt–O–Pd contribution identified in the second coordination shell confirms that Pt remains to a certain extent in the oxidized state. For the PtPd TAPN catalyst, a significant contribution of Pt–O–Pt coordination originating from a PtO₂-like structure was found. In this case, the possible formation of a PtO₂ layer on top of mono- or bimetallic nanoparticles is highly probable.^{25,53}

In contrast to the MFD and TAPN catalysts, no significant particle growth could be detected for the PtPd SDP sample after the hydrothermal aging step at 600 °C. Only an increase of the mean particle size from ~1.1 to 2.3 nm was measured, with a few larger agglomerates being found containing both Pt and Pd (Figure 9e). Additionally, both Pt and Pd were still

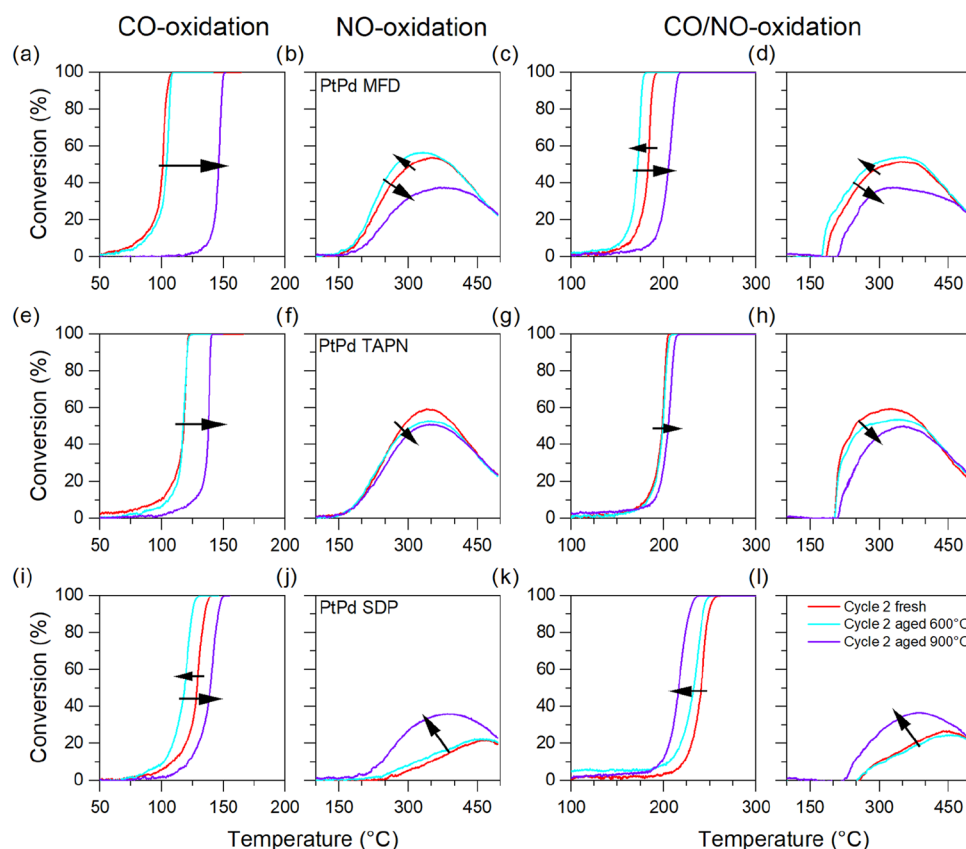


Figure 11. Catalytic activity for CO (a, e, i) and NO oxidation (b, f, j) and combined CO/NO oxidation (c, d, g, h, k, l) during the 2nd light-off cycle for the PtPd bimetallic samples in fresh state (red), after aging at 600 °C (turquoise) and after aging at 900 °C (purple).

present in oxidized state, as Pd^{2+} and Pt^{4+} species according to the LCA analysis of the XANES data in Figure 10. This electronic state could be explained by the smaller size of the noble metal entities in this sample, which are more sensitive to the air exposure during the cooling step of the hydrothermal aging experiment. The fitting of Pd K edge (Table S15) and Pt L_3 edge (Table S26) FT-EXAFS spectra also showed no clear difference between the fresh and aged catalyst states, resulting in almost identical coordination numbers for the different paths. Hence, the presence of highly dispersed and oxidized species with limited interaction between Pt and Pd in combination with a high surface alumina support seems to ensure a higher catalyst stability in this temperature range.

After hydrothermal aging at 900 °C for 16 h, more dramatic structural changes were observed with respect to the state and distribution of Pd and Pt species (Figures 9, S24, and S25). While variations were still noticed in the noble metal particle size distribution, biphasic structures consisting of a Pd-rich phase (Pt:Pd ratio between 1:4–1:10) and an almost equimolar Pt:Pd alloyed phase (Pt:Pd ratio between 1:1–1:2), closely attached, were recognized in all samples. The mean NM particle size in the three bimetallic samples after aging at 900 °C is ~ 34 nm for PtPd TAPN, ~ 60 nm for PtPd MFD, and ~ 36 nm for PtPd SDP catalysts. These results and especially the particle size distribution reported in Figure S22 indicate that even after aging at 900 °C, the PtPd TAPN and PtPd SDP samples still contain small noble metal NPs. In contrast, for the MFD catalyst, which initially comprised mixed bimetallic nanoparticles, only large noble metal particles were identified. The mobility of the Pt/Pd species on the catalyst's surface during the aging process seems to be increased once

both metals are present in a metallic state. This is driven in part by the expected lower Tammann/Hüttig temperatures of the alloyed phase relative to the pure Pt phase, which was found in the fresh PtPd TAPN and PtPd SDP catalysts. The *in situ* alloy formation after Pt and Pd autoreduction appears to cause a delay in the overall sintering kinetics.

Analogously to the 600 °C aged samples, the oxidation state of Pt and Pd in the 900 °C treated samples was investigated by *ex situ* XAS, and the LCA results are reported in Figure 10g and h. Further analysis of the EXAFS data is shown in the Supporting Information for Pd K (Tables S11, S13, and S16) and Pt L_3 edges (Tables S25, S27, and S29). The results obtained for the PtPd MFD, TAPN, and SDP catalysts suggest a clear similarity in their aging behavior at 900 °C. In all cases, significant contributions of Pd–Pt/Pt–Pd (alloy), Pt–Pt, and Pd–Pd (Pd-rich) paths were found, which correspond to a mixing/alloying extent of around 35% for Pd in all samples and up to 60% for Pt (Table S32). For all catalysts, a pronounced decrease in the oxidation state of Pt to the metallic state was noticed ($>90\%$ Pt^0 species, Figure 10). At the same time, over 50% of palladium was present in the metallic state, most probably alloyed with Pt. The remaining amount can be assigned to the observed PdO phase in the HAADF-STEM/EDXS images (depicted in Figure 9).

These pronounced structural changes were mirrored by the corresponding CO and NO oxidation activities. Figure 11 reports the catalytic performance of the three aged samples versus the CO, NO, and CO/NO conversions measured for the fresh samples during a second light-off/light-out cycle. Analogous to the fresh samples, a mild reductive pretreatment at 225 °C was also used in this case, which is not expected to

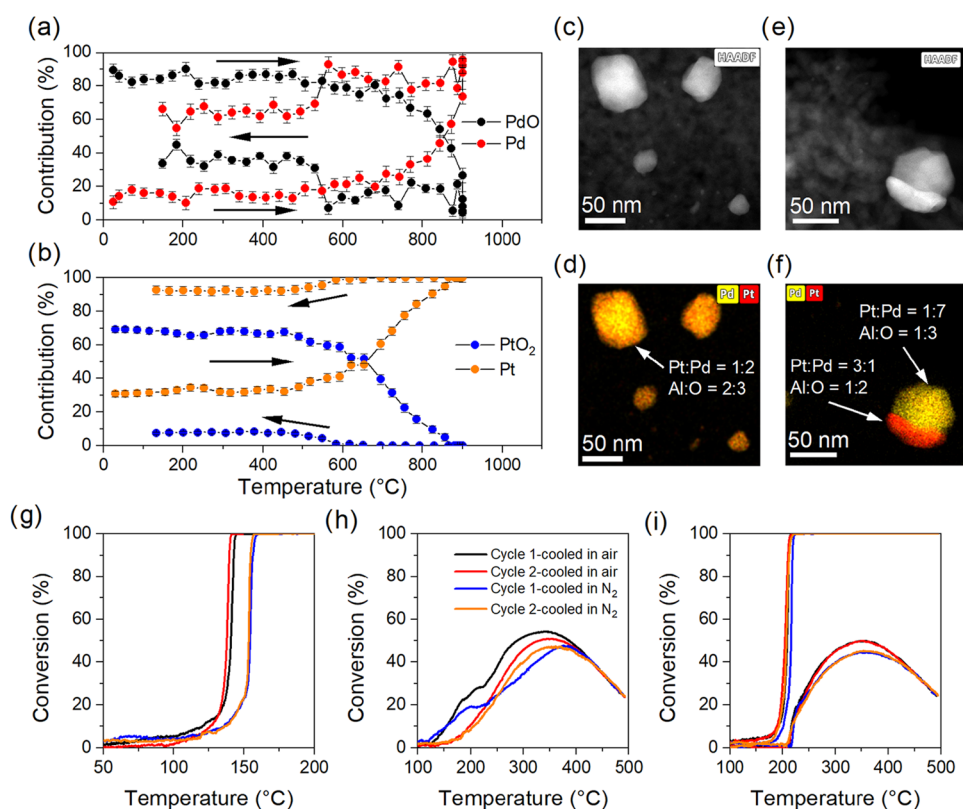


Figure 12. Results of LCA of the *in situ* XANES spectra measured at Pd K edge (a) and Pt L₃ edge (b) for the PtPd TAPN catalyst during heating to 900 °C with 10 °C/min in ~2.5% H₂O, 21% O₂, and He. STEM images and EDXS maps of the PtPd TAPN catalyst after hydrothermal aging at 900 °C and cooling in inert atmosphere (c, d), and after additional hydrothermal aging at 600 °C (e, f). Catalytic activity of PtPd TAPN after hydrothermal aging at 900 °C, comparing the samples cooled in air and nitrogen (g-i).

induce significant restructuring to the monometallic or bimetallic Pt- and Pd-based species. This is illustrated by the trends of the two consecutive light-off/light-out CO/NO oxidation cycles shown in the Supporting Information in Figure S18. After hydrothermal aging at 600 °C, which leads to the bimetallic particle segregation into separate alloyed PtPd particles and small Pd-rich nanoparticles, the PtPd MFD and PtPd TAPN catalysts showed a minimal decrease in the CO oxidation activity. At the same time, the PtPd SDP catalyst displayed an activity improvement, which can be related to the slight sintering of the noble metal NPs and formation of more active Pd species.³⁹ Analogously, the formation of slightly larger PtPd alloyed particles led to the increase of the NO-only oxidation activity for the PtPd MFD catalyst. In contrast, a slight decrease of the NO conversion was observed for the PtPd TAPN sample, and almost no variation was noticed for the PtPd SDP catalyst. In general, these trends in activity were maintained during the combined CO/NO oxidation. As platinum is generally considered the active element for NO oxidation,⁶⁹ these differences in activity can be correlated to the observed structural changes involving Pt-containing particles. In the case of the PtPd MFD catalyst, the NO oxidation activity in the presence of CO improved slightly, which could be due to the restructuring of the PtPd particles and possible migration of Pt atoms on the particle surface. The irregularly shaped NM particles present in the PtPd TAPN catalyst changed to more regularly shaped and larger particles (Figure 9), leading to the loss of active sites. As the Pt-containing entities in the PtPd SDP sample underwent only

minor structural changes, only a minor variation in activity was noticed during NO and combined CO/NO oxidation.

In line with the major increase in the noble metal particle size, a severe decrease of the CO oxidation activity was noticed for all samples after hydrothermal aging at 900 °C. A shift of the *T*₅₀ temperature of almost 50 °C was measured for the PtPd MFD catalyst. For the same sample, the NO conversion decreased to a maximum of 37% at 375 °C during the second NO oxidation cycle. The same effects were noticed during the combined CO/NO oxidation. The CO and NO oxidation performance decreased for the PtPd TAPN sample after aging at 900 °C, with a 23 °C increase in *T*₅₀ for CO oxidation and a drop from 59% to 50% in NO conversion maximum. At the same time, the decrease in CO oxidation activity is minimal during the combined CO/NO oxidation. The catalyst prepared by solvent-deficient precipitation (PtPd SDP) exhibited a decrease in CO oxidation activity (*T*₅₀ increase from 128 to 144 °C) but significantly higher NO conversion (36%). This tendency was also observed during CO/NO oxidation, although an improvement of CO oxidation was measured in this case: from a *T*₅₀ of 240 °C for the fresh catalyst state to 216 °C for the 900 °C aged PtPd SDP sample. Similarly, during NO oxidation, the conversion of NO reached a maximum of 36% for both cycles after catalyst aging. Overall, the NO oxidation performance of the bimetallic catalysts is promoted by the formation of sufficiently large Pt-rich nanoparticles⁴⁷ while the excessive particle sintering diminishes the total number of active sites.

Despite a clear correlation between the observed structural changes at 900 °C and catalytic activity, their underlying origin

remains inconclusive, considering the temperature range applied during hydrothermal aging. In general, the formation of large biphasic Pt–Pd nanoparticles comprising segregated alloyed and oxidized PdO phases has been described previously in the literature. Porter et al.²⁸ proposed that this biphasic morphology is responsible for the high stability of Pt–Pd/La–Al₂O₃ catalysts at temperatures up to 800 °C. However, since the autoreduction of PdO is expected to occur in this temperature range,⁶⁶ the formation of alloyed PtPd particles in a metallic state is anticipated at 900 °C. To elucidate the cause for the formation of biphasic structures, *in situ* XAS measurements at the Pd K and Pt L₃ edges were conducted in this study during heating of the PtPd TAPN catalyst to 900 °C and the subsequent cooling down under hydrothermal conditions. This sample was selected as representative for a more conventional synthesis method, which is easier to compare to previously published studies on similar systems. To simulate the hydrothermal aging conditions, a gas flow containing ~2.5% H₂O, 21% O₂, and He was dosed over the catalyst bed while applying a ramp rate of 10 °C/min. The results of the linear combination analysis of the XANES regions for the Pt L₃ edge and Pd K edge spectra are depicted in Figure 12a and b.

Despite the rather high heating rate of the catalyst bed, the autoreduction of platinum species was observed already above 500 °C, in line with previous literature data.⁶⁷ Under the conditions applied in this experiment, the rate of platinum oxide decomposition was almost linear, and the reaction was completed only at 900 °C. Metallic Pd⁰ formed to a notable extent only above 700 °C. Around 850 °C, over 50% of Pd species were present in a metallic state. Over the following 50 °C, another 25% of the remaining PdO_x species were converted to Pd⁰, while complete reduction occurred after reaching 900 °C. At 900 °C, both Pt and Pd were in a completely reduced state. However, this state is expected to be reached at lower temperatures during steady-state long-term aging procedures. After the expected formation of alloyed PtPd particles, the catalyst bed was cooled down to room temperature while maintaining the same gas mixture. In line with the study by Grunwaldt et al.,⁷⁰ Pd reoxidation was observed below 600 °C, whereas Pt remained predominantly in the reduced state down to room temperature with only minimal oxidation below 600 °C. This outcome confirmed the catalyst state indicated by the *ex situ* XAS data reported in Figure 10. Accordingly, the formation of biphasic Janus particles occurred due to Pd reoxidation and segregation during the cooling step after the hydrothermal aging at 900 °C. Considering the differences in the lattice structure, the tetragonal PdO cannot intermix with the face-centered cubic crystal lattice of the alloyed PtPd particles and therefore segregates at the boundary of the bimetallic particles. As PdO does not exhibit significant mobility below 600 °C, neither on the surface nor through vapor transport, it remained attached to the PtPd structure during cooling.⁷¹

To further validate the occurrence of these processes during catalyst aging, a separate PtPd TAPN sample batch was hydrothermally aged at 900 °C and cooled in N₂ to room temperature. According to the HAADF-STEM images and EDXS mapping shown in Figure 12c,d, no segregation took place by applying this protocol. Based on the EDXS spectra of the area comprising the noble metal particles, an Al:O ratio of 2:3 was determined. Since this ratio corresponds to the alumina composition, this result confirmed the presence of Pt

and Pd as metals in an alloyed state. The fitting of the FT-EXAFS data at the Pd K edge for this sample confirmed the presence of a stoichiometric homogeneous PtPd alloyed particles with a Pd–Pt neighbor ratio of $36 \pm 5\%$, which corresponds well to the NM loading. The detailed fitting information can be found in the EXAFS data section of the Supporting Information (Table S14). The sample hydrothermally aged at 900 °C but cooled in N₂ displayed a significantly lower NO and especially CO oxidation performance in comparison to the sample exclusively treated under oxidizing conditions (Figure 12g,i). In agreement with previous literature data,²⁸ the formation of biphasic PdO–PtPd structures could be correlated with the reasonable CO/NO oxidation activity exhibited even after catalyst aging under harsh conditions (Figure 12). This could be explained by the higher number of surface sites exposed by the biphasic structures, with the PdO phase facilitating CO oxidation and the Pt-rich alloyed phase promoting NO oxidation.

As illustrated by the *in situ* XAS data, the formation of the biphasic PdO–PtPd/alloyed PtPd structures is reversible at high temperatures. To check whether the complete segregation of sintered PtPd particles is achievable at lower temperatures, as observed during the hydrothermal aging at 600 °C for the as-prepared catalysts, the PtPd TAPN catalyst aged at 900 °C for 16 h and cooled in an inert atmosphere was additionally aged at 600 °C under hydrothermal conditions for the same duration. Figure 12e and f shows the STEM-EDXS images collected for the resulting aged sample. Whereas the expected formation of a biphasic Janus structure was confirmed, the complete segregation of these particles was not found. In the PdO-rich region, an Al:O ratio of 1:3 was found, confirming the excess of oxygen, while the Al:O ratio of 1:2 in the Pt-rich region suggests that only surface-level oxidation occurred for the Pt-rich zone. The high stability of the biphasic PdO–PtPd structure could be explained by the lower mobility of such large NM particles. Additionally, the support sintering and the onset of the γ -Al₂O₃ to θ -Al₂O₃ phase transition (Figure S20) could affect the PdO-support interaction and hinder its migration/redispersion.

4. CONCLUSIONS

A systematic investigation was conducted to unravel the influence of the initial structure of PtPd/Al₂O₃ catalysts on their activity and structural evolution during short- and long-term operation for CO, NO, and combined CO/NO oxidation. Conventional and advanced preparation methods were employed to obtain bimetallic catalysts comprising a broad spectrum of nanoparticle sizes, degrees of Pt–Pd interaction, and different levels of catalyst uniformity. In addition to conventional incipient wetness impregnation, advanced preparation methods were applied, including colloidal synthesis methods, supercritical fluid reactive deposition, flame spray pyrolysis, and solvent-deficient precipitation. Mild catalyst pretreatment procedures combined with complementary characterization methods were used to establish robust correlations between noble metal structure, sample surface and bulk composition, and catalytic performance. Based on extensive electron microscopy, XPS, *in situ/operando* XAS characterization, and catalyst testing, the following conclusions can be drawn:

- While several synthesis methods yielded a narrow particle size distribution, only the colloidal methods

ensured a uniform composition of PtPd particles and prevented the simultaneous formation of monometallic particles with limited Pt–Pd interaction as well as core–shell structures with Pt- or Pd-rich surfaces.

- The metallic state of the noble metals and particle size are key controlling factors for both the CO and NO oxidation reactions. Accordingly, the highest CO oxidation turnover frequencies were obtained after mild prereduction for catalysts containing metal particles with a surface-averaged size of >5 nm. For NO and combined CO/NO oxidation, the presence of a Pt-rich and alloyed surface further contributes to an enhanced catalytic performance.
- Based on extensive electron microscopy, XAS, and XPS investigations, a positive influence of the mixing/alloying degree was also found for catalysts containing noble metal particles with a surface-averaged size of <5 nm. Regardless of the pretreatment procedure, the PtPd MFD sample, comprising uniformly mixed/alloyed Pt–Pd particles, exhibited the highest turnover frequency for CO, NO, and combined CO/NO oxidation relative to other catalysts with NM particles in this size range.
- Under all tested reaction conditions, highly dispersed Pd and Pt species with limited interaction and present as very small particles showed the lowest catalytic activity, i.e., among bimetallic samples, the lowest average TOFs were measured for the PtPd SDP catalyst.
- The fingerprint of the synthesis method and initial catalyst structure was maintained throughout catalytic cycles up to 500 °C; only the oxidation/reduction of Pt and Pd species was found by *operando* XAS investigations for the PtPd MFD catalyst, without notable restructuring of the bimetallic particles.
- For applications involving moderate temperatures, such as stationary emission sources, hydrothermal aging at 600 °C was shown to induce PtO_x reduction. This process was accompanied by sintering and pronounced segregation of the bimetallic Pt–Pd particles into larger Pt-rich alloyed particles and smaller Pd-rich/PdO-like nanoparticles, with only minor impact on the catalytic activity. The catalyst prepared by solvent-deficient precipitation, initially containing small, highly dispersed Pt and Pd species, was the least affected.
- If the catalyst operation window extends to higher temperatures, the additional autoreduction of PdO is expected above 700 °C, as revealed by *in situ* XAS measurements. This process is followed by PtPd realloying and severe sintering of the noble metal particles, with pronounced impact on the catalyst activity. During long-term hydrothermal aging at 900 °C, sintering was less pronounced in samples with a lower uniformity of Pt–Pd interaction.
- The final catalyst structure is strongly affected by the cooling atmosphere after high-temperature exposure. Cooling from 900 °C in air favored Pd reoxidation and segregation from the PtPd alloy, leading to biphasic Janus nanoparticles composed of an alloyed PtPd phase and a Pd-rich mixed oxide phase. Cooling in an inert atmosphere preserved the PtPd alloyed particles but further contributed to the activity diminishment.

Overall, this systematic study advances an in-depth understanding of the behavior of bimetallic Pt–Pd catalysts across a

broad temperature range. The catalyst synthesis method, sample uniformity, as well as the evaluation by complementary characterization methods, were shown to be critical for deriving reliable structure–activity relationships for such complex systems. The insights gained into the structure of PtPd/Al₂O₃ bimetallic catalysts as a function of initial state, reaction temperature, and gas atmosphere can be used to further optimize the catalyst design and achieve more efficient noble metal utilization in other catalytic reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.6c04963>.

Additional characterization data is provided for all mono- and bimetallic catalyst samples (STEM-EDXS, XAS, XRD, XPS), including detailed parameters and results of the EXAFS data fitting, as well as additional activity data for CO and NO oxidation (PDF)

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Author Contributions

J.C. conducted the study, contributed to the catalyst preparation, and performed the catalyst testing, characterization, and related data analysis, and wrote the manuscript. P.D. and S.G. helped during catalyst synthesis and performed the XPS characterization. C.M. and R.P. performed the TEM and EDXS measurements and related data analysis. C.K. helped with the discussion of the TEM results. M.T., M.W., and S.B. helped during catalyst preparation. J.-D.G. helped during the design of the study and the discussion of the results. M.C. helped during the design of the study, and was involved in the XAS measurements, data discussion, and paper writing. All authors commented and gave input to finalize the manuscript.

Notes

Open Research: The data that support the findings of this study are available on the KIT open platform at: doi.org/10.35097/4eesdkf7mvg5we7p

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from the Deutsche Forschungsgemeinschaft DFG (German Research Foundation) via the SFB 1441 TrackAct – Project-ID 426888090 (Projects B01, B02, B03, C01, CN06). The authors acknowledge DESY, a member of the Helmholtz Association HGF, for the provision of experimental facilities and beamtime at P65 of Petra III. The authors would like to thank E. Welter for assistance during the experiments (proposal I-20221283). The authors acknowledge SOLEIL for the provision of synchrotron radiation facilities, and they would like to thank A. Zitolo for assistance in using the beamline “SAMBA” under proposal 20240773. The Swiss Norwegian beamline (BM31, ESRF) is acknowledged for the provision of beamtime, and their staff, specifically D. Stoian, for invaluable support. The authors thank the KIT light source (CATACT beamline) for the provision of synchrotron radiation for their studies. TEM measurements at INT were supported by KNMFi, a Helmholtz Research Infrastructure at KIT. The authors would like to thank A. Fisher for her help at the preparation of the ACAC and FSP catalyst, A. L. de Oliveira for the execution of the solvent-deficient catalyst preparation, Y. Träutlein for conducting the colloidal particle synthesis, and M. Crone for conducting the supercritical fluidic reactive deposition. T. Bergfeldt and the IAM-AWP team

(KIT) are thanked for conducting the ICP-OES analysis of the catalyst samples. M. Makowiak is thanked for conducting the BET-analysis at ITCP (KIT). A. Gaur and F. Maurer are thanked for their help during the XAS data analysis. Further thanks go to V. Marchuk, M. Kurt, S. Heck, and A. De Giacinto for their invaluable support during XAS synchrotron measurements.

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