

CO oxidation as a test reaction for strong metal-support interaction in nanostructured Pd/FeO_x powder catalysts

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Abstract:

A series of differently loaded palladium-iron catalysts was prepared by a controlled co-precipitation method of the nitrate precursors, in order to ensure homogeneous Pd particle size-distribution. After characterization of the pre-catalysts by various techniques, different controlled reduction conditions were applied to investigate the interactions within the Pd-iron system, containing reversible and irreversible processes like phase transformations, SMSI, sintering and alloying. Strong indications for the reversible surface decoration of the Pd nanoparticles with iron oxide species via strong metal-support interaction were found by the combined results of DRIFTS, CO-chemisorption, TEM and XPS measurements. This SMSI state was found to be unstable. It was observed independent of bulk phase or palladium particle size. Catalytic CO-oxidation was found to be a suitable test reaction for the study of the phenomenon: higher activity as well as oxidative deactivation of the SMSI state was observed by investigating the light-off behavior in repeated, temperature-programmed cycles as well as by isothermal measurements. The instability was found to be higher in case of higher Pd dispersion. In addition, bulk properties of the Pd-Fe system, like alloying, were investigated by detailed XRD measurements.

Keywords:

Palladium catalysis, CO oxidation, Pd/FeO_x, SMSI, DRIFTS, XPS, TEM, CO chemisorption

1. Introduction

Recently, iron oxide supported noble metal catalysts have been intensively studied as model systems for the effect of strong metal-support interaction (SMSI) in CO oxidation. For example, the group of Freund studied well-defined Pt-nanoparticles on Fe₃O₄(111)/Pt(111)[1–3]. The authors were able to generate SMSI (encapsulation) at elevated temperatures and to study its structure-function relationship. The support overlayer wetting the Pt-particles was identified by STM as a FeO (111) monolayer, because of a characteristic Moiré superstructure. In that state, a strongly enhanced CO oxidation activity was observed that was attributed by the authors to an oxygen-induced formation of a catalytically active O-Fe-O trilayer (Mars-van Krevelen type reaction mechanism). No such effect was observed so far for Pd/FeO_x model systems. Schalow et al.[4–7] studied the surface chemistry and reported the formation of different oxygen species on Pd/Fe₃O₄/Pt(111) model catalysts as

well as their influence on CO-oxidation activity. By combining surface sensitive IR-spectroscopy, XPS and molecular beam experiments, they found a reversible formation of Pd-oxide species at $T > 500$ K. It was dependent on the metal-support interface and occurred preferentially on Pd particles of about 7 nm in diameter. With regard to CO-oxidation kinetics, the Pd-oxides were found to suppress the reaction rate, when compared to adsorbed oxygen species. At $T > 450$ K the oxidation state of the Pd-species was found to be subject to dynamic changes, in dependence of the reaction gas composition. Wang et al.[8] reduced Pd/Fe₃O₄ with different reagents (H₂ or CO) and did not find any hints for encapsulation, but for the formation of bimetallic PdFe alloys, which have been characterized earlier by Felicissimo et al.[9].

These UHV-studies have been recently complemented by investigations in our group on more realistic catalysts[10,11]. Post-synthesis treatment of co-precipitated Pd/iron oxide catalysts was found to be crucial for the induction of phase-transition in the supporting iron oxide (from Fe₂O₃ to Fe₃O₄ polymorph). We were able to evidence the decoration of the palladium particles via SMSI upon reduction at 523 K by different techniques. The CO-chemisorption capacity of Pd in that decorated state was reduced and the reversibility of the overlayer formation was confirmed by in-situ XPS experiments. Activity studies of CO revealed an enhanced CO-oxidation rate in the state of decoration of the noble metal particles (E_a determined to 33 kJ/mol), as well as the instability of this SMSI state leading to fast deactivation during reaction ($E_a = 70$ kJ/mol)[11]. A possible explanation for the different behavior of the co-precipitated Pd/Fe₂O₃ catalysts, compared to the Pd/Fe₃O₄ model system could be release of oxygen during the phase transformation of the iron oxide support, which might facilitate the palladium encapsulation, as proposed by Wang et al.[8].

Other CO-oxidation studies on Pd/Fe systems like Pd/Fe₃O₄ core-shell particles[12], Pd/ α -Fe₂O₃[13] or evaporated model system[14] showed moderate catalytic activity with T_{50} values between 363 K[12] and 453 K[13] as well as a change of the crystal structure during reaction. The model system showed an E_a of 136 kJ/mol, decreasing with increasing reduction temperature. Much lower E_a (about 34 kJ/mol) and full conversion already at around 273 K was reported in studies using uncalcined, co-precipitated Pd/Fe(OH)_x systems[15–19].

The target of the present work was to get a deeper understanding of the formation, the reversibility and the stability of the decorated SMSI state during CO oxidation reaction, with a focus on the influence of the gas composition during reduction and during reaction. For this purpose, the analytical methods described previously[11] were applied and complemented by additional CO- infrared studies (DRIFTS) to probe the surface properties in different reduction states.

We present a multi-technique analysis to better understand the interaction of bulk and surface chemistry with the catalytic behavior in this complex catalytic system. We focus on the prehistory of the system that determines the nature of the active sites (chemical memory). Besides SMSI and PdFe alloy formation, processes like Pd particle sintering, Pd restructuring (by reversible hydride formation), Pd re-oxidation or poisoning by carbon species might play a role.

2. Experimental

2.1. Catalyst synthesis

The catalyst precursors were synthesized by co-precipitation from Fe- and Pd-nitrate solutions in an automated laboratory reactor and under controlled conditions. The details of the synthesis are presented as supporting information (SI). The precipitate precursor was dried in air for 24 h, mortared and calcined in 20% O₂/Ar atmosphere (2 h at 823 K, 2 Kpm heating rate). The product consists of PdO supported on α -Fe₂O₃ (hematite). The palladium loading was varied to yield 1, 2 and 5 wt.-% Pd/Fe₂O₃ catalysts. The calcined samples were reduced for microscopy studies in 5% H₂-Ar (100 ml/min) at different temperatures and with a heating rate of 2 Kpm and 30 min of holding time.

2.2. Catalyst characterization

Elemental composition of the samples was verified by optical emission spectroscopy (ICP-OES) and energy-dispersive x-ray spectroscopy (EDX). The specific surface area was investigated by nitrogen physisorption (BET). Scanning electron microscopy (SEM) was used to check the morphology, whereas transmission electron microscopy (TEM) was used to investigate the Pd particle distribution and monitor structural changes after treatments or reactions. The reduced samples were transferred to the microscope without air contact. X-ray diffraction (XRD) was used for analysis of the bulk structure/phase analysis. CO-chemisorption was performed to measure the active surface area. CO-IR measurements (DRIFTS), X-ray photoelectron spectroscopy (XPS) and thermogravimetry coupled with differential scanning calorimetry (TG-DSC) were applied to investigate surface and bulk properties during reduction and/or CO-oxidation. The equipment used and the detailed procedures are described in the SI.

2.3. Catalytic testing

The CO-oxidation as catalytic test reaction was carried out in a self-constructed catalytic reactor setup which is equipped with an on-line gas analyzer (X-Stream, Emerson/Rosemount) to quantify O₂, CO, CO₂ and H₂O. The temperature in the catalyst bed can be directly monitored by an analog connection to the gas analyzer. The setup is equipped with a switch-board for mixing the carrier gas (He 5.0) with CO (3.7), O₂ (5.0) or H₂ (5.0) with the help of 6-port switching valves (Valco, Vici). Every gas line is equipped with a filter, a mass-flow controller (E1-flow, Bronkhorst), a check valve and a shut-off valve. The CO-gas line is equipped with a carbonyl remover, consisting of a tube filled with inert SiC and heated to 573 K. The carrier gas line is equipped with a water and oxygen filter. The reactor itself is a U-tube reactor with an inner diameter of 5 mm, made of glass-lined steel (SGE). It is put inside a Cu-block oven for a maximum temperature of about 773 K, controlled by a Watlow thermo-controller unit and offering an isothermal zone of about 4 cm (+/- 1 K). The oven is equipped with a pressured-air connection to make faster cooling

possible. Usually, 25 mg of the catalyst, diluted by 250 mg of inert SiC (particle diameter: 250-355 μm) were weighed out and reduced in 5% H_2 -He or in 2% CO-He (100 ml/min) at different temperatures (2 Kpm, holding time 30 min.). For the subsequent CO-oxidation, normally three repeated light-off conversion cycles were measured (100 ml/min, 0.5% O_2 , 1% CO, 98.5 % He) from 323 to 523 K (2 Kpm heating rate, 15 min. holding). The TPR experiments were performed in the same setup using 5% H_2 -He and a heating rate of max. 5 Kpm. About 150 mg of undiluted catalyst were used for TPR.

3. Results

3.1. Synthesis and characterization of calcined pre-catalysts

Three Pd/Fe₂O₃ catalysts have been prepared by co-precipitation in the described synthesis reactor. For the surface study of SMSI, lower Pd loaded samples (1 and 2 wt.-%) were favored due to a more narrow Pd particle size distribution and to exclude particle size effects. A higher loaded 5 wt.-% sample was prepared in order to better investigate structural-chemical bulk effects during temperature programmed reduction.

Table 1 summarizes selected parameters of the pre-catalysts after calcination at 823 K. While the specific surface area of the lower loaded samples, which have been precipitated at pH = 4, were similar at about 35 m²/g, the higher loaded sample, prepared at pH = 9 as in reference[11], showed a value of 61 m²/g after calcination. All samples contained meso-pores with an average pore volume of 0.18 cm³/g and an average pore diameter of 22 nm according to BJH analysis. After calcination, the samples were investigated by SEM-EDX and XRD. EDX at different locations showed that the palladium distribution in case of all investigated samples was homogeneous. A porous structure was observed by microscopy, as shown in figures S2b and S3a. The iron oxide support phase consisted of crystallites of about 50 nm in diameter and was identified as the hematite polymorph, α -Fe₂O₃, as it can be seen in the XRD (figures S2 and S3 in supporting information). In the 5 wt.-% Pd/Fe₂O₃ catalyst, broad XRD peaks of PdO can be identified by Rietveld refinement as depicted in figure S3. The phase fraction of PdO was determined to 6.7 wt.-% which is in reasonable accordance with the nominal composition of about 6 wt.-% PdO.

3.2. Reduction of the calcined pre-catalysts – bulk effects

The general reduction chemistry of the PdO/Fe₂O₃ pre-catalysts was studied by TPR and is discussed based on the 5 wt.-% loaded samples in order to detect structural-chemical changes by XRD during reduction in different reducing environments, containing hydrogen or carbon monoxide.

Figure 1 shows a comparison of the TPR profile of the calcined sample, performed in 5% H_2 -Ar or in 2% CO-He after pre-drying in He at 573 K. It is notable in figure 1a that after a short activation period of about 0.5 min, the palladium oxide phase formed after calcination is

reduced instantaneously at room temperature by hydrogen, which is accompanied by a slight temperature rise indicating the exothermicity of the reaction. With increasing temperature, more water is formed which is an indication for Pd induced hydrogen-spillover that starts to reduce the surface of the iron oxide support, in good agreement to literature[20]. The bulk (hematite) reduction peak appears at about 525 K.

The theoretical calculated ratio between the first reduction signal (PdO-reduction) and the bulk reduction to magnetite is approx. 1:4.3 which is in reasonable agreement to the observed ratio of 1:4.8 if we take into account that the PdO reduction will overlap to certain content with spill-over reduction of the support. The state after the PdO reduction (at around 323 K) is referred to as the room temperature reduction (RTR) state in the following, while the state after hematite reduction at the end of the heating ramp will be called high temperature reduction (HTR). It is noted again that no sharp reduction signal is observed between RTR and HTR, but that a broad water signal is detected indicating surface reduction in that temperature region. We will show later that the formation of an SMSI overlayer occurs already at sub-HTR temperature and assign these broad signals tentatively to formation of an SMSI-state. In case of reduction in H₂ the SMSI formation process seems to occur continuously by spill-over.

Interestingly, this is different from the reduction profile performed in 2% CO (Fig. 1b). Besides the RTR and HTR signal, two other signals can be observed, one at 415 K and the other at 466 K. A third, smaller signal appears at around 380 K. Peak integration (not shown) revealed that Pd oxide reduction in that case is only complete after the signal at 415 K, likely due to different Pd species present. In order to better monitor the degree of Pd reduction, TG-DSC experiments were performed that numerically confirmed complete PdO reduction in case of hydrogen atmosphere already at room temperature, compared to 398 K in case of CO (Fig. S4), which is in reasonable agreement with the CO-TPR peak found at 415 K. Furthermore, support reduction by spill-over was confirmed.

A first attempt to characterize the sample state at the respective TPR peaks in the different reduction atmospheres was done by XRD of the 5 wt.-% catalyst. Scans performed after RTR in hydrogen atmosphere indicated that the iron oxide phase was still hematite while the palladium oxide was reduced to metallic palladium, supported on α -Fe₂O₃. The size of the particles was very small, indicated by the broad XRD peak. As shown previously for hydrogen reduction, the HTR peak is due to reduction of the support from hematite to magnetite phase, Fe₃O₄[11]. After HTR, magnetite formation was also confirmed by XRD in case of reduction with CO.

XRD after reduction in CO atmosphere was performed before and after the central TPR peak at 466 K in order to obtain information about possible structural changes during this reduction step (Fig. S5). Both diffractograms were found to look very similar. The bulk iron oxide phase in both cases is still hematite, while the palladium is in its metallic state. No obvious changes in the crystal structure during the formation of SMSI upon reduction could be detected, indicating that the formed overlayer will be x-ray amorphous or too small to be detected by XRD. The diffractogram of the same sample after 523 K reduction in CO atmosphere shows reflections for palladium, supported on magnetite, while partial alloy formation cannot be excluded (Fig. S6).

The RTR state of the catalysts reduced in hydrogen was investigated by CO-chemisorption,

XRD and TEM. The average Pd particle diameter, as determined by CO-chemisorption (Tab. 1), increased with increasing palladium loading, from 1-2 nm (1 wt.-% sample) until about 5-6 nm (5 wt.-% sample). The calculated active metal surface area increased from 2.6 m²/g (1 and 2 wt.-%) until 4 m²/g (5 wt.-%). The particle sizes determined by chemisorption are not exactly the same as if determined by microscopy, which might be due to the fact that chemisorption is an integral method, different to TEM. On the other hand, in case of CO-chemisorption different assumptions have to be made when calculating the average particle diameter, like particle shape, adsorption stoichiometry (binding geometry of the CO-molecule) and the maximum coverage for a monolayer of CO adsorbed on palladium, that is known not to exceed values of $\Theta = 0.3-0.5$, dependent on the surface orientation of ideal Pd surfaces[21]. In fact, after RTR of the 1% sample (see Fig. 2a), only sub-nm sized, highly dispersed Pd clusters can be observed in STEM. The TEM image (bright field) and the STEM image (high angle annular dark field - HAADF) of the 2 wt.-% catalyst were recorded after 473 K reduction in order to investigate not only the Pd distribution but also possible surface reduction effects. The images show homogeneously distributed, round shaped palladium particles of about 2 nm in diameter, as dark dots in the first, and white dots in the latter case (Fig. 2b+c) confirming the uniform distribution of Pd in the co-precipitated catalysts. Fig. 2b shows a HRTEM image at a state of the catalyst between RTR and HTR, where surface reduction by spill-over hydrogen was proposed.

Indeed, an amorphous overlayer can be seen at the surface which is interpreted as a hint for a partially reduced surface of the hematite support. Fig. 2d presents a STEM image of the 5 wt.-% sample also after 473 K reduction. Homogeneously distributed Pd particles in the size of about 4 nm can be seen, but no overlayer.

One possible state of PdO/Fe₂O₃ after reduction not considered so far is the formation of Pd-Fe alloys, which can show markedly different catalytic properties compared to non-alloyed Pd[22,23]. Bulk sensitive XRD has been applied on the 5% catalyst to check for alloy formation at HTR. To regulate the formation of an alloyed reference state for these experiments, higher reduction temperatures than 523 K have been applied. Figure 3 shows the Rietveld-fitted results after reduction at 523 K (HTR) and after 723 K. While after HTR, the only bulk phase present is magnetite, the amount of further reduced species, namely alpha iron, is significant after 723 K reduction (about 10 wt.-%). In both cases the palladium phase has been fitted with the ICSD-633135 reference for the cubic intermetallic compound Pd₃Fe. It has to be noted that there is a close structural relationship with metallic palladium (fcc structure) and that this structural model can be used to satisfactorily fit both phases in the present case due to the poorly crystalline and nano-sized nature of the Pd phase. Thus the lattice parameter has to be carefully evaluated in order to discriminate non-alloyed Pd and the intermetallic. In addition to the lattice parameter change, the increase of the fitted amount of the Pd phase from about 4% at 523 K to about 6% after 723 K reduction is another indication for progressing alloy formation in this temperature regime. It is worth noting that the Pd reflection remains broad, even after 723 K reduction, which is an indication for the prevention of substantial sintering. In order to further study the alloying, the Pd lattice parameter 'a' has been monitored, using the literature parameter of 3.89 Å as a reference for metallic Pd[24] and five phase pure reference alloys with a known composition between Pd₉₅Fe₅ and Pd₇₅Fe₂₅ (i.e. Pd₃Fe), prepared by melting of the elements. From these

references, a Vegard plot (Fig. S7b) has been created to calibrate the amount of iron in the palladium particles of the 5% catalyst after different reductive treatments. The lattice parameter contracts with on-going incorporation of iron: the first scan of the sample, after reduction in 5% H₂ at RT exhibits a lattice parameter of 3.889 similar to the literature value for metallic palladium[24]. Already after HTR (523 K), the parameter has decreased to 3.859 Å, representing a formal composition of Pd₃Fe, according to the Vegard plot. After further reduction at 623 K only a small decrease of the lattice parameter to 3.848 can be detected, representing still Pd₃Fe composition. With further increase of the reduction temperature to 723 K the lattice parameter decreases until a value of 3.815 which represents, according to the plot, a formal composition of PdFe. However, according to the XRD pattern, the structure in that state would still be cubic Pd₃Fe. The differences between the bulk reference materials and the catalysts are likely affected by the nano-structured nature of the Pd phase in the latter and by the poor crystallinity leading to ambiguous diffraction data.

3.3. DRIFTS surface investigation

IR spectra of CO probe molecules have been measured in different reduction states of the 2 wt.-% (Fig. 4-5) and the 5 wt.-% (Fig. 6) Pd/Fe₂O₃ catalysts.

For the first part of the IR-measurements, the 2 wt.-% sample has been reduced at 323 K in a 5% H₂-Ar mixture for 30 min. to simulate RTR conditions. Remaining hydrogen and produced water were purged with argon and a mixture of 2% CO in argon (100 ml/min) was introduced into the chamber to study the CO adsorption on the reduced palladium sites (Fig. 4, left side). Spectra have been recorded after 10 min, 30 min, 1h and 1.5 h. Gas phase CO is visible between 2100 and 2200 cm⁻¹. The IR band at 2081 cm⁻¹ can be assigned to linearly adsorbed CO on metallic palladium.[25–27] At the beginning of exposure, a shoulder at 2035 cm⁻¹ is visible. This is probably due to geometric reasons: a high CO coverage reduces the back-bonding capability and leads to a blue-shift. A second prominent signal is visible at 1952 cm⁻¹ which represents the carbonyl band for bridged-bonded CO on Pd.[25–27] Due to a broad signal below 1900 cm⁻¹, even some abundance of threefold coordinated CO on Pd cannot be excluded.[28,29] These observations confirm that the surface properties of the state after RTR resembles dispersed, but unmodified Pd. The same sample has been reduced afterwards in 5% H₂-Ar at 473 K (2 Kpm) and flushed again with argon after cool down to room temperature. Then, 2% CO was dosed again to the sample for about 115 min. The recorded spectra are shown in figure 4 (right side). Mostly gas phase CO could be detected, with a very small signal of CO species on Pd (2081 cm⁻¹) in the shoulder. Purging with argon eliminated the gas phase signal and no remaining band was observed.

Afterwards CO-oxidation conditions (1% CO, 0.5% O₂) were simulated in the DRIFTS setup in order to study the influence of the kinetic measurements on the IR properties of the reduced samples. The temperature was increased with 2 Kpm until the maximum reaction temperature of 523 K (hold 30 min.) while CO₂-formation could be detected in the IR-spectra, indicating the proceeding reaction.

During cooling-down, spectra were recorded. At about 370 K, CO adsorption starts again and

the appearance of three dominant signals between 2101 and 2155 cm^{-1} that have not been observed in the measurement before CO-oxidation (Fig. 4) are observed as soon as the sample temperature falls below 373 K (Fig. 5). Besides some gas phase CO present in this measurement design and physisorbed CO on palladium (at around 2150 cm^{-1})[25], the adsorption of CO on Pd^{2+} is very likely to contribute to the spectrum.[29–32] Nevertheless, CO on metallic Pd (1979, 1945 cm^{-1}) is present as well.

The CO-adsorption properties of the 5 wt.-% sample were investigated at 77 K, after in-situ reduction in 2% CO-Ar atmosphere at 423 and 473 K, to compare the two surface states before and after the TPR-signal at 466 K (see Fig. 1). In addition, the support Fe-O-vibration region has been monitored. The results are presented in figure 6 (a,b) and in figure S8 (Fe-O vibrations, SI).

Again, linearly and bridged bonded CO at wave numbers of 2093 and 1976 cm^{-1} were observed. That is an indication for the presence of metallic palladium after 423 K reduction (Fig. 6a). In addition to that a small shoulder at around 2152 cm^{-1} can be observed after this first reduction step which can be explained by linearly adsorbed CO on some little amounts of residual, not yet reduced PdO that appears at 2150-2160 cm^{-1} according to literature.[29,31–37] After 473 K reduction, the signal for adsorbed CO decreased to less than 10% (Fig. 6b), similar to the study after hydrogen reduction. Compared to 423 K reduction, also the Fe-O-vibration intensity of the support has reduced after 473 K reduction and disappeared completely after further increase of the reduction temperature to 523 K (Fig. S8, SI). The fact that even cooling to 77 K did not induce any measurable CO adsorption on the reduced catalyst suggests that the formation of surface alloys at this temperature (473 K) is rather unlikely because literature reports adsorption signals in the observed region for CO on various Pd alloys.[38,39]

3.4. CO chemisorption measurements

To quantify the decrease of active metal surface area the samples containing 1% and 2% Pd were also studied by volumetric CO chemisorption at 313 K after reduction at 323 K (RTR) and 473 K. The active surface area was calculated from the capacity of strongly adsorbed CO, as mentioned before. The adsorption isotherms are plotted in figure S9a (2% sample) and S9b (1% sample, both SI). The typical behavior for saturation of the surface with strongly bonded CO can be seen after RTR (Fig. S9a, panel a). With increasing pressure only the amount of physisorbed CO increased. After reduction at 473 K the CO-chemisorption capacity drastically decreased, but is partly restored with increasing pressure (panel b).

In order to test the reversibility of this effect, the sample was re-calcined and measured for a second time after RTR and successively after 473 K-red. (Fig. 9a, panels c+d). For the 1% sample (Fig. S9b) the decrease after 473 K reduction in comparison to the RTR is similar.

Re-calcination in both samples partially restored the initial, higher chemisorption capacity, but the total adsorbed volume decreased by 12% for the 2% sample and by 40% for the 1% sample, compared to the original CO uptake: in case of the 2% sample the monolayer capacity was determined to 27 $\mu\text{mol/g}$ and the active surface area was calculated to 2.6 m^2/g in the RTR state, with a dispersion of 29% (cubic particles assumed). After 473 K red. the

values decreased to 8 $\mu\text{mol/g}$ and 0.7 m^2/g . After the re-calcination procedure the capacity (RTR-state) again reached values of 24 $\mu\text{mol/g}$ and decreased again to 10 $\mu\text{mol/g}$ (after second 473 K red.). Langmuir constants were determined in case of the first RTR state ($K = 2.3/\text{mbar}$) and the first 473 K red. state ($K = 0.4/\text{mbar}$), however these values have limited physical meaning due to the fact that earlier calorimetric measurements on a similar sample in our group (see Fig. S9c+d) showed restructuring of the active sites is likely to start at CO pressures of 0.5 mbar already while the first data point of the chemisorption measurements is at 2-3 mbar.

3.5. CO oxidation experiments

In a first kinetic experiment, the isothermal reaction rate for CO_2 -formation was studied over the 2 wt.-% catalyst at 430 K, after performing 473 K-reduction (5% H_2 -He). Two complete CO-oxidation cycles between RT and 523 K were performed before the measurement, in order to minimize irreversible effects (Fig. 7, inlay). During the third ramp the temperature of 430 K was kept constant for 300 min (Fig. 7, curve 1). Afterwards the sample was re-reduced at 473 K and the isothermal measurements were conducted again at 430 K, but this time during the first CO-oxidation ramp (blue curve, no. 2). After another 300 min the procedure was repeated (curve no. 3).

As it can be seen, the catalyst is in a kind of deactivated state after the initial CO-oxidation cycles were performed (curve 1) with a CO_2 production rate of about 85 $\mu\text{mol g}_{\text{Pd}}^{-1}\text{s}^{-1}$ and with little further deactivation upon time. In contrast to that, the isothermal CO_2 formation rate is much higher (almost 250 $\mu\text{mol g}_{\text{Pd}}^{-1}\text{s}^{-1}$) directly after the next reduction step (curve 2). However, the activity decreased fast with ongoing reaction until values that were even slightly lower than those of the first deactivated state.

The transient activation effect was found to be reversible as the sample was re-reduced for the second time: the rate increased again until values only slightly lower than after the first re-reduction (200 $\mu\text{mol g}_{\text{Pd}}^{-1}\text{s}^{-1}$) and showed a similar deactivation behavior during the isothermal measurement. Obviously the reduction at sub-HTR temperature of 473 K created a state of the catalyst that is much more active in CO-oxidation but that is also highly instable in the reaction atmosphere on the other hand.

In order to study the activation and deactivation behavior on the differently loaded Pd catalysts and its dependency on the reduction conditions in greater detail, the reactivity in CO-oxidation was determined in form of repeated, temperature-programmed reaction studies, so-called “light-off” curves. The performance of the catalysts in the individual reaction cycles was evaluated and compared based on the temperature of 50% conversion (T_{50}) as well as the conversion at 425 K (X_{425}). The parameters are summarized in table S2. The results for the 1 wt.-% loaded catalyst are presented in figure 8.

In the first panel (a), the measurement after RTR (323 K) in 5% H_2 is presented. The sample has a comparably high initial activity but gradually deactivates with repeated reaction cycles. The second panel (b) shows the performance of a fresh sample, after 473 K – reduction in hydrogen. While the change of the reaction parameters with cycling is similar to RTR, a significant difference can be seen in the shape of the first reaction curve especially at low

temperature.

In order to disentangle reversible and irreversible effects, the deactivated state, which is very similar in both experiments, independent of the pre-treatment, has been chosen as a more suitable reference state than the fresh catalyst. Therefore the same sample shown in panel b has been re-reduced (RTR, 323 K) in order to obtain a stable and metallic state of the catalyst. It can be seen in panel c that after this treatment the sample performs relatively stable with very similar T_{50} and X_{425} values compared to those found for the first measurements, indicating that all irreversible processes have been completed.

This state of the catalyst was further studied with regard to the reversible effects. It was re-reduced according to the TPR (Fig. S12) at a sub-HTR temperature of 410 K to set surface decoration of the Pd particles without bulk reduction of the support. Interestingly after this treatment, X_{425} increased to 15% in the first oxidation cycle before decreasing again close to the value observed before (Fig. 8d). No difference in T_{50} can be detected between the cycles. The fast deactivation can be notably seen as the curve after pre-treatment bends and approaches those of the following cycles with increasing temperature and conversion. Only the activity increase seen as the difference between the curves at low temperatures can be safely assigned to the effect of the reducing pre-treatment. The procedure has been repeated (Fig. 8e) in order to confirm the reversible promotion. Finally, the activation energy (Fig. 8f) of the deactivated state of the catalyst was determined in a temperature range of 395-425 K to about 56 kJ/mol, which is in the range reported for metallic palladium[21].

A comparative study with a different reducing agent (CO instead of H_2) and a test of higher reduction temperatures to study possible alloy formation effects was conducted based on the 5 wt.-% catalyst (Fig. S10). The catalytic data of the 2 wt.-% loaded sample after reduction in H_2 or CO were in general similar to those of the 1- and 5 wt.-% catalysts and can also be found in the SI (Fig. S13).

The TPR of the 5 wt.-% Pd/Fe₂O₃ catalyst was discussed in section 3.2 (Fig. 1) already. We recall that during reduction in CO additional TPR peaks were detected between RTR and HTR at 415 and 466 K which were not detected using hydrogen.

For the first two measurements (Fig. S10a,b) a reduction temperature (2% CO) of 423 K was selected, to achieve a catalytic state present after the first reduction peak. The experiments look qualitatively similar to those of the 1% sample, but the 5% sample is clearly more active. In the first measurement the deactivation after three cycles (Fig. S10a) is more pronounced than after repeated reduction (Fig. S10b). Here, the initial high activity of the first cycle is only restored to some extent while the second and third cycles are identical which shows that the stable deactivated state was reached.

This is different from the sample that has been measured after reduction at 473 K, in a state after the second reduction peak (panels c+d): the two repeated measurements look almost completely identical with a much more active first reaction cycle. Again, the state was highly instable, though there was little further deactivation recorded between the second and the third cycle. After repeated measurements with the 473 K reduced catalyst, the activation energy in the deactivated state was determined in a range of 395-425 K again which remained in the same range (60 kJ/mol), similar to the 1% sample. Both CO-reduction treatments at 473 K and the E_a extrapolation can be found in SI (Fig. S14).

After HTR (523 K) of a fresh catalyst (Fig. S10e) the difference between first and last

reaction cycle is less pronounced again. The second and the last cycle are completely overlapping, showing that all kinds of reversible or irreversible processes have finished already after the first cycle. This behavior is more pronounced after reduction of the catalyst at 573 K (panel f): this time, the first cycle is less active at higher temperatures, but still most active at lower temperatures. The second cycle is least active. This can be an indication for counteracting, overlapping processes.

3.5. XPS investigation before and after CO oxidation

To better connect the structural analysis and the catalytic data, the surface properties of the deactivated reference state and the highly active state formed during reductive pre-treatment of the catalysts were studied by XPS.

The development of the Pd3d core-level signal of the 1% and 2% Pd/Fe₂O₃ samples was investigated at the HZB synchrotron facility during a temperature programmed reduction procedure. As mentioned, the samples were not in the as-prepared (freshly calcined) state anymore, but had already been reduced at 473 K and successively measured in CO-oxidation (3 cycles, 373-523 K, as described in the kinetic part). Under UHV conditions a first surface sensitive XPS scan at a kinetic energy of 150 eV (about 1 nm of information depth) was recorded. As it can be seen for the 2% sample in figure 9 (lower part), most of the Pd3d signal resembles oxidic palladium (337.4 eV, FWHM = 1.99), with additional content of metallic Pd at 335.7 eV (FWHM = 1.38; Pd3d_{5/2}). The binding energy values are slightly higher compared to literature values because of the particle size effect that leads to an up-shift due to the small Pd particles in our case [18,40–42]. Peak fitting showed that the oxidic content was 66 %. After TPR (until 473 K; 0.4 mbar H₂) and further increase of the hydrogen partial pressure to 10 mbar at 473 K for 1h, the palladium oxide got reduced. As it can be seen in figure 9 (upper part), most of the palladium is in its metallic state (335.8 eV, FWHM = 0.95) now (71%). At 336.6 eV (FWHM = 1.50) another palladium species can be fitted that we tentatively attributed to SMSI. As reported for similar metal-oxide interfaces[4,43–45] the palladium at the particle surface can be shifted to higher binding energy when being in contact with an iron oxide overlayer. The integrated amount of the new species of 29 % would exactly represent the content of Pd atoms at the surface of the particles in the present Pd particle size, according to the dispersion calculation. Surface alloys like PdFe would also show an energy up-shift, depending on the treatment conditions as described in the literature [46–50], but our IR data did not confirm alloy-induced shifts in the CO wave numbers as reported for example by Felicissimo [9] or Wu et al. [23].

In order to confirm enrichment of iron oxide species on the palladium particles during the reduction process, the intensities of Pd and Fe at the surface ($E_{\text{kin}} = 150\text{-}200$ eV) and in the bulk (700-800 eV) were integrated at different stages of the reduction, as summarized in table S1 (supplemental). The results are depicted in figure 10: the atomic ratio of Pd : Fe near the surface before the reduction was 3.1 to 96.9 and decreased until 2.0 to 98.0 after reduction (2% sample). In comparison to the surface, the ratio in the bulk stayed almost constant (2.4 to 97.6 before and 2.5 to 97.5 after reduction). In case of the 1% sample the results were comparable. With ongoing reduction, segregation of iron oxide on the palladium particles

was confirmed.

As for the changes in the iron oxide support phase between the deactivated and the freshly reduced state of the 2% sample, we refer to the NEXAFS part (Fe L absorption edge, supporting information, Fig. S11). C1s spectra of the same sample before and after in-situ reduction are presented in Fig. S15: during reduction, the amount of carbonate species formed during the CO-oxidation decreased.

4. Summary and Discussion

In our work we investigated the structural changes in the bulk as well as on the surface of homogeneous, co-precipitated Pd-iron oxide powder catalysts with different palladium loadings during reduction under various conditions and their influence on the catalytic activity in CO-oxidation. All samples were synthesized in a controlled way with a uniform particle size distribution. Therefore size-dependent differences among one investigated sample can be excluded. We were able to find a clear indication for the formation of surface decoration on all differently loaded catalysts depending on the reduction temperature or medium. This SMSI effect was found to be reversible and it was observed independent of bulk phase changes, alloy formation or irreversible processes like sintering or deactivation by possible by-product (e.g. carbonate) formation.

By DRIFTS- and CO-chemisorption measurements, it could be shown that the adsorption capacity for carbon monoxide in the state after reduction at 473 K (both for hydrogen and CO-reduction) got decreased to almost zero, while no additional crystalline phase could be detected in XRD. Re-calcination restored the adsorption capacity by 88% (2% sample) and by 60% (1% sample) compared to the initial capacity. The higher palladium dispersion apparently increases the sensitivity for irreversible deactivation processes like agglomeration. It was shown in the TPR and TG experiments that spill-over plays a significant role in case of hydrogen atmosphere leading to a continuous reduction of neighboring iron oxide around Pd particles. This increases the mobility and wetting probability of the support and leads to an overgrowth of reduced iron oxides onto the palladium. In contrast to that reduction in CO atmosphere was associated with a separate peak and did not induce SMSI-formation before 423 K. HR-TEM images in the 473 K reduced state confirmed the formation of an amorphous overlayer.

XPS investigation of the 1% and 2% samples by hands of a performed depth profile confirmed an overgrowth of iron oxide support over the palladium particles which was concluded due to a reduced Pd:Fe ratio at the surface with ongoing reduction, in contrast to the unchanged bulk ratio. In case of the 2% sample, detailed fits of the XP-spectra after CO-oxidation measurements compared to those in an in-situ reduced state revealed the presence of metallic and oxidic palladium in the deactivated (reacted) state while the presence of a second palladium species shifted to higher binding energy compared to metallic Pd in case of the freshly reduced state delivered further proof for surface decoration, probably by an Fe-O layer, in analogy to the Pt/FeO_x model system [1,4]. The amount of the new species was identical with the Pd dispersion determined by CO chemisorption. XPS further confirmed the presence of carbonate species after the CO oxidation measurements as well as their decrease

upon reduction.

Palladium oxide formation during the kinetic measurements was also confirmed by DRIFTS (Fig. 5) and by the reduction profile after the reaction (Fig. S12). However the influence of that process on the activity was limited (Fig. 8c). The structural results (XRD) upon increased reduction temperature showed the possible formation of a PdFe alloy, most likely in the structure of Pd₃Fe but with increased iron content (iso-structural substitution). It started to form only at temperatures higher than 473 K, most likely at the surface. At 473 K, IR experiments however did not confirm alloy formation. NEXAFS spectra of the reduced sample after CO oxidation revealed that most of the support is in the hematite phase, with increasing magnetite content during in-situ reduction.

The surface decorated state led to a transient high activity in CO-oxidation, which is in agreement with earlier studies of the SMSI phenomenon [1,4,5,11]. Furthermore, the high volatility and reversible re-formation of the SMSI state during a second reduction step at sufficiently high temperatures was confirmed. The degree of volatility apparently also depends on the palladium particle size that is in a direct correlation to the palladium loading: electronic conditions at the metal-support interface in case of sub-nm sized palladium particles present on the 1% sample, lead to a faster oxidative destruction of the overgrowth layer. After several reaction cycles and minimization of irreversible processes, the deactivated state after SMSI destruction was found to be relatively stable, with only moderate further deactivation, probably by carbonate formation. The higher initial activity (first reaction cycle after RTR) is attributed to a higher Pd dispersion and agglomeration during the reaction. The activity of the 5% sample in general was higher compared to the other samples due to a higher BET surface area and a higher Pd surface area.

While the instability of the SMSI state prohibits its industrial application in sustained CO-oxidation, this reaction overall was found to be a suitable test reaction for the convenient study of reactivity and stability of the SMSI phenomenon and decouple it from the other, above-mentioned processes. Though it could be shown that the formation of SMSI is occurring independently of the phase transformation of the bulk hematite phase into the magnetite polymorph or alloying, such processes nevertheless play an important role with regard to activity decrease in the kinetic measurements of CO-oxidation, probably by limiting the metal-support interface. The activation energy of the deactivated samples was comparably low but in the range of literature values for metallic palladium [11,21].

5. Conclusion and Outlook

The present study revealed that careful CO-oxidation can be applied to detect the specific chemical state of the catalyst. The variations in the present data as well as in the literature are a sign for the chemical dynamics of the system and not of the unsuitability of the CO-oxidation reaction as a chemical spectrometer for the reactivity of a Pd catalyst under ambient conditions. The special case of Pd/Fe will be extended to other catalytic systems in the effort to verify a generic character of the method.

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Figure Legend:

Fig. 1: TPR-curves (RT-573 K) of the 5% sample in 5% H₂ (a) and 2% CO (b).

Fig. 2: STEM image of the 1% Pd sample after RT-reduction (a), TEM-image (b) and STEM-image (c) of the 2% Pd sample after 473 K reduction and STEM image of the 5% Pd sample after 473 K reduction (d). Pd particles and support overlayer in red frame are marked in blue and green.

Fig. 3: XRD of 5% sample recorded at RT after in-situ reduction at 523 K (a) and 723 K (b) in 5% H₂. Insets: magnification of region between 65 and 90°.

Fig. 4: CO-DRIFTS spectra of 2% Pd/Fe₂O₃ after 323 K-red. (left) and 473 K-red. (right).

Fig. 5: DRIFTS of the 2% sample after re-oxidation in 0.5% O₂ + 1% CO (523 K).

Fig. 6: DRIFTS study of 5% Pd sample: CO-desorption spectra measured at 77 K after 30 min reduction in 2% CO/Ar at 423 K (a) and at 473 K (b).

Fig. 7: CO-conversion and reaction rate in isothermal CO-oxidation measurements at 430 K over the 2% catalyst after deactivation (1, red curve) and after two times of re-reduction (blue curves, 2+3). Two complete oxidation cycles after 473 K reduction performed before (inset).

Fig. 8: CO-oxidation curves of the 1 wt.-% catalyst after reduction in hydrogen atmosphere at RT (panel a) and at 473 K (panel b, fresh sample), followed by RTR (c), repeated reduction at 410 K (same sample, d,e) and activation energy measurement in deactivated state (f).

Fig. 9: Pd3d signal of 2% Pd/Fe₂O₃ sample at $E_{\text{kin}} = 150$ eV in deactivated state (lower panel) and after in-situ reduction (upper panel).

Fig. 10: surface and bulk Pd/Fe ratio of the 1% (blue bars) and 2% (red bars) sample, before and after reduction.