

# Strong Metal-Support Interaction and alloying in Pd/ZnO catalysts for CO oxidation

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## Abstract:

Pd/ZnO catalysts with different Pd content have been synthesized, thoroughly characterized and investigated with regard to their reduction behavior in hydrogen or carbon monoxide containing atmospheres, by applying CO-chemisorption, photoelectron spectroscopy, X-ray diffraction, electron microscopy, TPR and DRIFTS techniques. As a catalytic test reaction, CO-oxidation has been applied. The interaction of the noble metal with the support has been revealed in a way that can distinguish between alloying and other surface spreading/wetting phenomena, induced by strong metal-support interaction (SMSI). It was found that while alloy formation promoted CO-oxidation activity additional ZnO<sub>x</sub> formation by SMSI had the opposite effect. Zinc enrichment at the surface was detected during reduction of the catalysts, depending on the reducing agent and the Pd particle size.

Keywords: Palladium, Zinc oxide, CO-oxidation, SMSI, alloying, XPS

## 1. Introduction:

The catalytic system of zinc oxide supported palladium catalysts has attracted broader scientific interest since Iwasa et al. [1] tested a number of Pd catalysts in methanol steam reforming (MSR,  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$ ) that was discussed with regard to hydrogen production for vehicles [2–6]. They showed high activity and selectivity for the reaction on Pd/ZnO, whereas Pd on irreducible supports only led to the decomposition of methanol to CO and hydrogen. When Iwasa et al. [7] reduced Pd/ZnO up to 773 K, they observed further improved selectivity (>98%) which they attributed to the formation of the intermetallic compound (IMC) PdZn, proven by XRD and XPS. Since then, a lot of studies have been performed to understand the specific electronic properties as well as the geometric structure of these Pd/ZnO based catalysts with regard to their catalytic performance in general, and for methanol steam reforming, which have been summarized in two recent reviews by Föttinger [8] and Armbrüster [9] et al. The most common synthesis method comprises treatment of ZnO-supported Pd systems, which were prepared e.g. by impregnation or co-precipitation in atmospheres that contain hydrogen or other reducing gases at elevated temperatures. When studying the reduction behavior of a 10 wt.-% Pd/ZnO catalyst, Hong et al. [10] reported a H<sub>2</sub> consumption peak maximum at about 673-700 K, representing ZnO support reduction and PdZn formation, which was confirmed to be complete at 773 K by XRD. Furthermore, hydrogen spill-over was reported already below 360 K which indicates that surface reduction

can start much earlier. Iwasa et al. [7] confirmed PdZn formation by observing a broad TPR-peak at 500-750 K as well as XRD reflections when reduced at 623 K. In photoelectron spectroscopy upon reduction, the monitored Zn *LMM* Auger spectra showed a shoulder ascribed to intermetallic zinc at 493 K already, representing further evidence for ZnO surface reduction with hydrogen in the presence of palladium. PdZn reflections in XRD patterns were reported at 523 K already by Tew et al. [11]. Chin et al. [12] studied 5-20 wt.-% Pd/ZnO catalysts by TPR and were able to observe a shift of the reduction peak maximum to lower temperatures, by decreasing the loading. With regard to the electronic properties, Pd3d XPS studies have been performed by several groups upon the alloying process [7,13–18].

Recent studies on high-temperature prepared PdZn with a varied Pd-content (47-59%) by Friedrich et al. [19] were able to show the importance of the Zn-content for MSR selectivity due to the changing electronic properties (Zn-rich samples lead to a higher binding energy for the Pd3d signal in XPS). They could show that bulk Pd also has an influence on the Zn/Pd ratio at the surface, the Pd3d binding energy and the amount of oxidized Zn-species at the surface, that were shown to be important for high activity in MSR. Both, electronic (ligand-) and geometric (ensemble-) effects play a role when talking about the influence of the IMC formation process towards CO-adsorption in IR spectroscopy [18,20–22]. By FTIR and EXAFS, Föttinger et al. [22] confirmed the IMC formation on Pd/ZnO under MSR conditions or upon reduction at 623 K as an ongoing process, proceeding from the outer part of the Pd particle to the inner part, as well as the reversibility of this mechanism by oxygen treatment at 573 K, leading to a formation of metallic Pd and ZnO islands on-top of the pre-formed PdZn-overlayer. Such kind of surface decoration was also studied by Hong et al. [10] who investigated the Pd/ZnO system in terms of SMSI [23]. They proposed a schematic model in which the on-going reduction (also by spill-over) would lead to  $\text{ZnOH}_x$  and  $\text{ZnO}_{(1-x)}$  species around the more and more flattened Pd particles with an increasing metal-support interface, that would, with increasing reduction temperature start to form the PdZn alloy from the bottom to the top of the Pd particle. After reoxidation (e.g. by exposure to air for sample transfer), also ZnO islands as well as PdO on Pd would form and the  $\text{ZnO}_{(1-x)}$  species would be partially reoxidized, as far as accessible [24]. Metal-support interactions were also tested on various supported Pd catalysts for methanol synthesis [25].

In SMSI state, catalysts have been reported to be more active for certain reactions like CO-oxidation [26]. Due to the simplicity of that reaction it can be used as a test reaction to characterize also the Pd/Zn/ZnO-system. For example, Iwasa et al. [27] were able to show the highest selectivity for preferential oxidation of CO in the presence of hydrogen (PROX) on the Pd/ZnO, after PdZn formation. Small amounts of  $\text{H}_2$  in the feed gas were able to enhance the CO-conversion. The IMC formation was discussed to be responsible for a reduced CO binding energy that made  $\text{O}_2$ -adsorption more competitive. The same observations were made by Johnson et al. [28] who investigated CO-oxidation and CO-adsorption on  $\alpha$ - and  $\beta$ -PdZn and observed 5-10 times higher initial rates for the reaction, compared to pure Pd, however observing also deactivation upon time by zinc oxidation. CO-oxidation in general was intensively studied and discussed as a suitable model reaction for various heterogeneous, catalytic processes [29]. In the present work we study the role of SMSI in the Pd/ZnO system, by applying a similar, methodological approach, recently applied on the Pd/ $\text{Fe}_2\text{O}_3$  system [30]: the change of activity for CO-oxidation during SMSI/alloy formation as well as the

reversibility by reoxidation will be investigated and compared to the changing structural and electronic characteristics.

## 2. Experimental

### 2.1 Catalyst synthesis

The catalyst precursor was synthesized by co-precipitation, as described earlier [30]. The use of the co-precipitation technique was motivated by the idea that synthesis through a bulk-like distribution of the precursor species might give rise to more uniform metal-support interaction without favoring specific surface sites of the support as sometimes encountered when using the impregnation technique. Therefore, 650 ml of a diluted (0.1 M) solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar) were prepared and mixed with a solution of calculated amounts of  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , that had been dissolved in 3g  $\text{HNO}_3$  (65%) in 100 ml  $\text{H}_2\text{O}$  (sample 16688) or with purchased Pd-nitrate solution (8.3 wt.-% Pd-content in 10 wt.-%  $\text{HNO}_3$ , Alfa Aesar) in case of the samples 15657 and 16120.

Precipitation occurred drop-wise with 0.4 M NaOH solution in an automated reactor-system (Labmax, Mettler-Toledo), which contained already about 400 ml of deionized water. During the precipitation (acid solution addition rate of 6 g/min), the pH-value (pH = 7.5), temperature ( $T = 298 \text{ K}$ ) and stirring rate ( $r = 300 \text{ rpm}$ ) were monitored and kept constant in order to assure the most similar conditions and chemical potential for every forming crystallite and thus the best possible product homogeneity. After precipitation, the product was aged for 1 h (100 rpm, RT), filtered and washed three times (3x 1l of demin. water) until conductivity of the solution was  $< 0.01 \text{ mS}$ . The solid, pale yellow product was dried in air for 24 h (298 K), mortared and calcined under controlled conditions in 20%  $\text{O}_2 - \text{Ar}$  atmosphere (2 h at 623 K, 2 Kpm heating rate). The ochre product consists of PdO supported on hexagonal ZnO. The palladium loading was varied to yield catalysts with 0.75, 2.5 and 5 wt.-% Pd/ZnO. For the 5% sample, a metal solution of 0.2 M and a precipitation pH-value of 9 were used.

### 2.2 Catalyst characterization

Elemental composition of the samples was assessed by optical emission spectroscopy (ICP-OES) and energy-dispersive x-ray spectroscopy (EDX, to rule out contaminations). Total surface area was investigated by nitrogen physisorption (BET). Scanning electron microscopy (SEM) was used to check the surface morphology, whereas HR-TEM and STEM was used to investigate the Pd particle distribution and monitor structural changes after treatments or reactions. X-ray diffraction (XRD) was used for analysis of the bulk structure/phase analysis. CO-chemisorption was performed to measure the active surface area and to detect support spreading/wetting (decoration of the Pd-particles). CO-IR measurements (diffuse reflectance infrared fourier-transform spectroscopy, DRIFTS) and photoelectron spectroscopy (XPS) was applied to investigate electronic surface properties during reduction and/or CO-oxidation. For experimental details we refer to the supporting information section.

### 2.3 Catalytic testing

The CO-oxidation as the catalytic test reaction was carried out in a self-constructed catalytic reactor setup, described earlier [30]. Usually, 25 mg of the catalyst, diluted by 250 mg of inert SiC (particle diameter: 250-355  $\mu\text{m}$ ) were weighed out, first reduced in 5% H<sub>2</sub>-He (100 ml/min) at 323 K (2 Kpm), holding time 30 min. TPR in 5% H<sub>2</sub>-He or in 2% CO-He were performed usually at higher temperatures and with max. 5 Kpm heating rate. For CO-oxidation, normally three repeated light-off conversion cycles were measured (100 ml/min, 0.5% O<sub>2</sub>, 1% CO, 98.5 % He) from 323 to 523 K (2 Kpm heating rate, 15 min. holding time and 0.5 Kpm for cool down to 373 K (1h holding time).

## 3. Results and Discussion

### 3.1 Synthesis and characterization

Table 1: physical parameter of the investigated, calcined catalysts

Nr.	Catalyst	Pd-loading (ICP-OES) (wt.-%)	BET surface area (m <sup>2</sup> /g)	Average Pd particle diameter <sup>a</sup> (CO-chem.; nm)	Active surface area (m <sup>2</sup> /g) <sup>a</sup>
15657	0.75% Pd/ZnO	1.6	40	2.5	3.1
16688	2.5% Pd/ZnO	3.9	39	6.1	3.2
16120	5% Pd/ZnO	4.6	43	6.7	3.5

<sup>a</sup>after 323 K-red.

The precursor synthesis for the Pd/ZnO catalysts was performed via a controlled co-precipitation approach. The pH-value during precipitation with NaOH did not fluctuate much due to buffer effects. No pH-change upon 1h of ageing time could be observed as presented in figure S1. After washing and drying the pale yellow precipitate was calcined leading to the formation of PdO on ZnO, hand in hand with a color change to ochre, depending on the loading. Surface studies of SMSI and CO oxidation were conducted with the two lower loaded (0.75 and 2.5 wt.-%) samples due to an expected more narrow Pd particle size distribution, higher dispersion and reflectivity (HR-TEM, DRIFTS) to exclude particle size effects. To better monitor bulk chemical changes (XRD), the highest loaded sample was used. The 2.5 wt.-% sample was chosen for XPS studies in order to combine sufficiently high loading and dispersion. CO chemisorption was applied as connecting method for the 2.5 and 5 wt.-% samples. Some physical parameters of the differently loaded samples after calcination are shown in table 1: the nominal palladium content of the samples was determined by ICP-OES measurements while the content of the two lower loaded samples was found to be higher than expected. The BET area of all samples is in the range of 40 m<sup>2</sup>/g. Meso-pores were found in all samples. Regarding the influence of the palladium content on the average particle size, the chemisorption measurements revealed a particle growth with increased noble metal loading, from about 2 nm for the 0.75 wt.-% samples, to almost 7 nm for 5 wt.-%. Due to some assumptions like shape factor of the particles and the content of

CO-molecules that can be adsorbed for example in bridged binding-geometry, small differences between the sizes determined by microscopy might arise. Nevertheless, microscopy measurements (see part 3.4) of the lowest loaded sample confirmed the chemisorption results. The calculated active surface area of the catalysts was very similar with about 3.1 to 3.5 m<sup>2</sup>/g. The reduction behavior of the samples will be discussed in the next section.

### **3.2 Chemical and structural behavior of the system during reduction (2.5 and 5 wt.-% sample)**

Since strong metal-support interaction is a phenomenon that depends on the reducibility of the catalyst support [23], temperature-programmed reductions of the samples have been performed. For reduction, a 5% hydrogen – helium gas mixture as well as a mixture consisting of 2% CO-He has been applied and the results were compared. Furthermore the structural changes during the reductive heat treatment were monitored by XRD as well as by transmission electron microscopy (part 3.4). The higher loaded samples (2.5 - 5 wt.-%) were selected for the TPR and XRD measurements due to the comparably high detection limit of phases in XRD.

The TPR curves are depicted in figure 1. In case of the hydrogen gas mixture as reducing agent (C,D), water formation is visible already at room temperature which can be ascribed to reduction of palladium oxide to metallic palladium. With increasing temperature the water peak shows a shoulder due to the drying effect. Until the end of the temperature program (723 K), a continuous amount of water is detected that can be ascribed to spill-over reduction of the zinc oxide support surface [36], while only a very smooth increase of the water signal could be detected at 671 K (C). In order to better work out the temperature dependence of possible processes like alloy formation or the formation of reduced zinc oxide species (SMSI), the measurements have been repeated with the milder reducing agent CO (A,B), showing a more nuanced reduction profile. It is noted that in other precursor systems like Pd acetate complexes it was observed that CO does not necessary act as a mild reducing agent, but can also lead to bigger Pd particles [37]. CO dependent on the precursor, reduction in CO can also lead. Both samples show an initial increase of the CO<sub>2</sub> formation at the beginning (PdO reduction) while the respective signal in case of the higher loaded sample is less pronounced, which is unexpected and might be explained by an incomplete reduction at this state. With increasing temperature a large CO<sub>2</sub> peak arises at 450 K (A) respectively 475 K (B) with a smaller second peak/shoulder at 507 K (A) respectively 522 K (B). The general appearance of the two differently loaded samples in the TPR experiments is similar, with increased amounts of CO<sub>2</sub> and water formed proportional to the higher palladium loading. In order to assign the observed signals to specific reduction processes further experiments like XRD were performed, applying pre-reduction temperatures observed by the TPR-experiments. After the temperature programmed reduction of the 2.5 wt.-% sample in 2% CO-He, to 473 K in the XRD setup, the Rietveld fitted diffractogram of the sample (figure 2A) shows reflections for the hexagonal ZnO phase as well as for metallic palladium, represented among others by a broad signal at 40 ° for the Pd 111 plane. By comparing the results of the XRD measurement after 473 K and the TPR, one can conclude that the

formation of probably partially reduced zinc oxide support does not yet lead to detectable alloy formation in the presented case. This is different from the higher loaded sample (5 wt.-%) that has been also investigated by XRD after CO-reduction until 623 K, in the state at the end of the TPR curve (Fig. 1B). In that case, the alloy PdZn (ICSD 180143) has been formed as shown in figure 2B. Different to the lower loaded sample, the XRD of the higher loaded one has been measured after the reduction processes that are represented by the shoulder at 522 K. Therefore it could be concluded that a most likely amorphous (due to the missing additional phase component information), partially reduced zinc oxide compound forms on the surface during the reduction in the CO-containing atmosphere, and that later, with further increase of temperature, the alloy formation process goes on. Another explanation would be that the alloy formation starts at the surface but cannot be detected as long as it has not yet proceeded sufficiently to the bulk.

Though the different Pd particle sizes present in the two different samples allows us to assume different interaction with the support, integration of the CO-TPRs revealed that the CO<sub>2</sub> amount formed in both cases was larger by a factor of 2.5 compared to the amount that would form by PdO reduction alone. This would fit to the formation of PdZn covered by additional reduced species. However the formation of carbon species in that case cannot be excluded.

In addition to the mentioned studies, pseudo in-situ XRD measurements were performed on the 2.5 wt.-% Pd/ZnO sample, reducing the sample in the XRD sample holder in hydrogen containing gas mixture at increasing temperatures and successively measuring the diffraction patterns at room temperature (to exclude thermal effects), in order to further study the behavior of the system with regard to (bulk)- alloy formation.

As it can be seen in figure S2 (supporting information), the formation of a PdZn alloy compound upon reduction in a 5% hydrogen containing atmosphere starts between 573 K and 623 K, indicated by the magnified region that shows the prominent 101 and 110 reflections of the compound at angles of about 41 and 44 °. With further increase of the reduction temperature the signals get sharper due to PdZn crystallite growth.

### **3.3 Influence of reductive treatments on the activity in CO-oxidation**

In order to investigate the influence of the described reduction procedures of the catalysts on the catalytic performance in CO-oxidation and to be able to compare the structure function relationship, two differently loaded catalysts, the 0.75% and the 2.5 wt.-% samples have been selected. The temperature at 50% conversion ( $T_{0.5}$ ) and the conversion at 425 K ( $X_{425}$ ) are compared as reaction parameters (Table S2). Figure 3 shows the kinetic measurements for the lower loaded sample (three repeated TPO-cycles for each measurement) after reduction in CO-containing atmosphere and according to the previously determined TPR (Fig. 3, first panel). It can be seen that when being reduced at a temperature below the first peak in the

TPR (423 K, state at position 1), the catalyst is less active in the first CO-conversion cycle, compared to the others.

From the activation behavior it can be suspected that the palladium species might not have been completely metallic after reduction in CO at 423 K or that some carbon species, formed upon reduction might become decomposed during the oxidation which might lead to a kind of re-dispersion. After reduction in CO containing atmosphere at 523 K (in the valley between the two TPR peaks), the first conversion cycle shows a lower slope and a more active catalytic system compared to the following cycles. When being repeated (reduction at 523 K and CO-oxidation cycles with the same sample), the catalytic behavior is exactly reproduced, only experiencing a negligible deactivation due to irreversible processes. When measured in state 3, after the reduction at the highest temperature, 673 K, the first conversion cycle still shows a slightly higher CO-oxidation activity, though the difference between the first and the following cycles is not so pronounced anymore as in case of the repeated measurements after 523 K reduction. Obviously the activating processes upon reduction must have been counteracted by some kind of other process, probably delimiting the active surface area. The activation energy which was determined in the deactivated state of the catalyst after 623 K reduction (after the three conversion cycles), was 49 kJ/mol however, similar to earlier determined values of 42-60 kJ/mol [30].

In case of the higher loaded sample (Fig. 4), hydrogen containing reducing atmosphere has been applied and CO-oxidation runs were repeated twice, each time after reduction at 473 K (panels A+B). A similar reversible process of activation in the first cycle and deactivation upon CO-oxidation, compared to the lower loaded sample, reduced in CO atmosphere, was observed with exactly the same values for  $T_{0.5}$  and  $X_{425}$  for runs A+B. When a fresh batch of the sample was reduced until 573 K, the behavior was very similar again, the sample only experiencing slight deactivation (Fig. 4C). Another measurement with a fresh catalyst was performed after reduction at 723 K, where according to the TPR-profile of the sample (see Fig. 1C) further changes should occur (Fig. 4D). At this high reduction temperature all palladium should be in the PdZn state already, according to the XRD-measurements. Nevertheless the TPO profile still shows the first cycle being more active than the other cycles, though with a pronounced overall deactivation, probably due to sintering or other irreversible effects like carbonate formation. The activation energy determined after the cycles (Fig. 4E) was higher than the one in case of the lower loaded sample, namely 82 kJ/mol. For further comparison of the influence of the reducing atmosphere, one measurement with a fresh amount of sample after reduction in 2% CO-He, also at 473 K, has been conducted, presented in the last panel (Fig. 4F): the influence on position and shape of the first and the second curve was negligible, but the sample is slightly less active than in case of the hydrogen which might be explained also by the difference, CO and hydrogen show with regard to reactivity towards the palladium (dissolving probability, re-dispersion and hydride/carbon formation effects). Catalytic measurements for the 5 wt.-% sample showed similar trends.

A plate-like, porous structure of the calcined 0.75% Pd/ZnO sample with crystallite diameters of about 40 nm can be observed in the SEM micrograph presented in figure 5a. The HAADF-

STEM image of the same sample after reduction in hydrogen atmosphere at 323 K is presented in figure 5b. In that mode, it is possible to distinguish the metallic palladium from the oxide support due to its much higher atomic number. The particles are depicted as bright grey spheres with almost uniform size in the image and are homogeneously distributed. The size of about 2-3 nm for the lowest loading confirms the CO-chemisorption results, presented in table 1. Since the size and distribution of the palladium particles in that sample was found to be appropriate to study the processes previously discovered by the TPR and catalytic measurements in greater detail, some amount of the sample has been reduced at 623 K in 5% CO/Ar gas mixture, similar to the kinetic experiment (Fig. 3) and transferred to the TEM without air-contact. Figure 5 c-e presents a series of images taken from one specific region of the sample, where a palladium particle in exposed position at the support surface could be found. By variation of the focus of the microscope, we were able to identify a zinc oxide over-layer covering the palladium particle as well as parts of the support. That would be an explanation for the further decrease in activity found in the kinetic studies in that state. A slight astigmatism might also be present in panels c-e. Though it was not possible to directly study the PdZn lattice parameter by microscopy, according to our XRD-experiments and supported by the kinetic studies, such small Pd particles should be alloyed already almost completely. Based on that observation we propose a model scheme in figure 5f, where the palladium after 623 K reduction is present as PdZn, covered by a partially reduced ZnO<sub>x</sub> over-layer (SMSI). To further proof the over-growth, surface sensitive investigations (IR, XPS, chemisorption) were performed.

### **3.5 Electronic and structural surface investigations: reversible formation of SMSI over-layer versus alloying**

#### **3.5.1 DRIFTS:**

Due to the benefit of a low palladium loading on reflectivity in general, the highly dispersed 0.75 wt.-% Pd/ZnO sample studied by electron microscopy has also been selected for the diffuse reflectance infrared measurements. The sample has been reduced in-situ by a mixture of 2% CO in Argon (30 min.) at increasing temperatures, according to the TPR-profile, presented in figure 3, first panel, and infrared spectra after adsorption of CO at liquid nitrogen temperatures (77 K) were recorded during desorption by pressure decrease. The first reduction took place at 323 K, where most of the palladium present is expected to be in its elemental state, and successively the sample got reduced and was measured at 523 K and afterwards at 623 K, in the state of the HR-TEM images. The respective Kubelka-Munk spectra are presented in the following figure 6 (A-C):

After reduction of the sample at 323 K in the CO-Ar gas mixture, pure CO is flushed in at liquid nitrogen temperature and gets adsorbed on the noble metal. Besides the typical vibrational features for CO linearly bonded to metallic Pd (2093 cm<sup>-1</sup>) and bridged bonded to metallic palladium (1977 cm<sup>-1</sup>), a palladium species at 2150 cm<sup>-1</sup> is present on which CO



weakly bonds and desorbs again with decreasing partial pressure. The vibrational frequencies observed in our study are in agreement with literature values for CO linearly and bridged bond on metallic palladium [18,20–22,36,38], supported on zinc oxide as well as for linearly bond CO on oxidic palladium (PdO, 2150 cm<sup>-1</sup>).

After 323 K reduction, most of the Pd is in its metallic state with a minor content of palladium oxide. After reduction of the sample at 523 K (cf. after the first reduction peak in the TPR-profile of figure 3) and CO-adsorption again at 77 K, the wave numbers for the linearly and bridged bond CO on the palladium species got shifted towards lower numbers, namely 2085 cm<sup>-1</sup> and 1970 cm<sup>-1</sup>. This red-shift has been reported earlier [8,38] and is typical for the electronic modifications that take place during alloy formation. Compared to metallic palladium, a negative partial charge of Pd in PdZn is present and therefore the capability to electron back-donation into anti-bonding states of the CO-molecule that weakens the C-O-bond, increases.

The total intensity of the adsorbed CO got slightly decreased during the higher temperature reduction, without significant changes in the intensity ratio between linearly and bridged bond species. Literature reports a decrease of bridged bond species with increasing formation of intermetallic PdZn [38] due to the increasing distance between two palladium atoms which would get too large for the CO-molecule. Therefore, Pd segregation seems possible. Another measurement after reduction at 573 K was performed revealing complete reproducibility of the results. After the third reduction step at 623 K (after the second reduction peak in the TPR-profile) however, the signals for CO on palladium or palladium-zinc alloy have completely disappeared – only gas phase CO is detected. This is a clear indication for the formation of a ZnO<sub>x</sub> over-layer which has been formed on the metal through the influence of strong metal-support interaction and inhibits CO to get adsorbed onto palladium. The measurements therefore confirm our observations of the covering of the palladium particles by hexagonal zinc oxide (Fig. 5) as well as the slight decrease of activity in the CO-oxidation measurements compared to a lower reduction temperature (Fig. 3) and support the hypothesis that alloy formation - at least in case of the lowest loaded sample – starts before complete decoration of the sample with a reduced support over-layer. Similar processes were reported by Föttinger et al. [22] who confirmed the IMC formation on Pd/ZnO during MSR conditions or upon reduction at 623 K as an ongoing process, proceeding from the outer part of the Pd particle to the inner part, as well as the reversibility of this mechanism by oxygen treatment at 573 K, leading to a formation of metallic Pd and ZnO islands on-top of the pre-formed PdZn-overlayer.

### 3.5.2 XPS:

In order to study the surface decoration effects as well as electronic surface modifications XPS measurements after reductive and oxidative in-situ treatment have been performed using two different kinetic energies of the photo-electrons for accessing different information depth. Furthermore, the shift in the binding energy during the treatments was monitored in order to detect electronic modifications due to possible alloy formation. For the photoelectronic studies the 2.5 wt.-% Pd/ZnO sample was investigated to understand the

differences between the cycles observed in kinetic measurements (Fig. 4). A part of the probe was pre-reduced in the kinetic measurements setup (473 K in 5% H<sub>2</sub>-He gas mixture, sample 16949) and transferred to the XPS setup with the help of a vacuum transfer box to avoid air contact. Another batch was deactivated by 3 CO-oxidation cycles (373-523 K, common reaction conditions) after the pre-reduction at 473 K (16957). Table S1 and Fig. 7 summarize the results of the integrated peak areas of the Pd3d and the Zn3d core levels and at two different information depths ( $E_{\text{kin}} = 200$  and 800 eV). It can be noted that the Pd/Zn ratio stays more or less the same if the photoelectrons are being emitted from deeper regions, namely 4.5 to 5.7 percent of palladium independent of the treatment. The situation is different at surface near regions ( $E_{\text{kin}} = 200$  eV): The batch that has been pre-reduced and transferred to the XPS chamber shows a Pd:Zn ratio of 7.6 to 92.4 (UHV-measurement at RT). The sample that was in its deactivated state, showed a much higher Pd-content at the surface with 12.7%. When being reduced in-situ inside the XPS chamber (0.4-2.5 mbar H<sub>2</sub> partial pressure, maximum 2h at 473 K), the palladium content at the surface got reduced more and more until similar values that were discovered in the pre-reduced sample. That could be an indication for surface decoration and for the reversibility of the decoration process, since both measurements show very similar results, or an indication for reversible surface alloying, as described earlier [8] which would also lead to a decrease in the Pd/Zn intensity ratio.

After the UHV measurement of the pre-reduced sample at room temperature, a temperature programmed CO-oxidation procedure was conducted in the XPS-chamber (RT-473 K, 5 Kpm heating ramp) with a total gas pressure of 0.3 mbar and a flow of 1 ml/min of oxygen and 2 ml/min of CO in order to simulate the conditions of the light-off experiments. Figure S6 (supporting information) shows the Pd3d signal ( $E_{\text{kin}} = 200$  eV) during the experiment, with in-situ scans at 300, 343, 408 and 473 K. Increasing CO<sub>2</sub> formation was detected by mass spectrometry with increasing temperature, as expected. A continuous shift of the palladium signal to lower binding energies is visible with ongoing oxidation and increasing temperature which is a hint for the instability of the (alloyed) surface state formed during the reduction towards oxidative conditions.

Due to the monitored changes in the electronic behavior, alloy formation is expected to play a role at least at the surface, when the system is being reduced under the executed conditions. Regarding figure 8, we can discuss the energy shift as well as the composition of the palladium species in more detail: in the freshly (in-situ) reduced state (1h at 473 K), the energy shift is most pronounced with a peak maximum (3d<sub>5/2</sub>) at 335.7 eV. The shape of the peak is symmetric, both being an indication for PdZn alloy formation [19]. The fit suggests that about 5% of Pd remained in its metallic state. The spectrum of the pre-reduced sample (16949) shows that the alloy must already partially decomposed during the transport (PdZn: 56%, Pd: 34%, PdO: 10%). The binding energy shifted to lower values (about 335.5 eV). Decomposition could lead to formation of ZnO islands covering the Pd and leading to a similar Pd/Zn surface ratio as compared to the in-situ reduced state [24].

After CO-oxidation (deactivated sample 16957 measured under UHV-conditions at RT) the signal got shifted to even lower binding energies and closer to those expected for metallic

palladium (335.2 eV) [39]. Also the shape of the signal indicates the presence of a single metallic species [40]. The composition was estimated to be 34% PdZn, 57% Pd and 9% PdO.

The binding energies are in good agreement to literature [19,36,41,42]. While Iwasa et al. [7,13] reported a shift in the Pd 3d<sub>5/2</sub> signal of 0.1 eV by reduction of a 10 wt.-% Pd/ZnO catalyst from RT to 493 K, attributed to metal-support interaction, and of further 0.6 eV to 335.9 eV between 573 and 673 K reduction, Zsoldos et al. [14] reported an increase of the binding energy by 1 eV to 335.85 eV in between 420 and 880 K reduction of a 8.5 wt.-% catalyst. Earlier, Wehner et al. [15] noticed a reversible shift of the binding energy of a 2 wt.-% Pd/ZnO catalyst after 523 K reduction in hydrogen (336 eV), exposure to air at RT (335.5 eV) and repeating the 523 K reduction. This reversibility was confirmed by their Zn *LMM* Auger measurements by a shoulder at higher  $E_{kin}$  in the reduced state, representing the intermetallic compound. More recent measurements confirmed the alloying process in aerosol-derived PdZn particles [16] (335 eV  $\rightarrow$  335.7 eV) and by monitoring the Zn3d peak [17]. A difference from metallic palladium (335 eV) to monolayer PdZn (335.3 eV) and multilayer PdZn (335.8 eV) has been reported by Rameshan et al. [18].

Details to the fit components presented in figure 8 are listed in the following table 2. The higher FWHM of Pd after CO oxidation might indicate the presence of small amounts of zinc and/or carbon species incorporated into Pd or particle restructuring.

Table 2: parameters of the fitted Pd3d species

	component	binding energy / eV	content / %	FWHM / eV
in-situ red.	Pd	335.1	4.8	0.9
	PdZn	335.7	95.2	1.1
pre-red.	Pd	335.1	34.0	1
	PdZn	335.7	55.8	1.2
	PdO	336.5	10.2	1.5
after CO- ox.	Pd	335.0	57.3	1.4
	PdZn	335.5	33.9	1.2
	PdO	336.7	8.8	1.5

### 3.5.3 CO-chemisorption:

As a third surface sensitive technique and following to earlier studies of the SMSI phenomenon [26,30] the chemisorption of carbon monoxide has been applied to investigate the total uptake of CO on the noble metal surface, calculate its dispersion and study the dependence of the chemisorption capacity on the reduction of the system. Similar to these studies, the CO-chemisorption capacity of the Pd/ZnO system markedly reduced when the catalyst had been treated in reducing atmosphere at elevated temperatures. In this case the 2.5 % sample has been measured after reduction at 323 K (in hydrogen gas mixture), measured again after reduction at 623 K, re-calcined at 573 K (30 min.) in 20% O<sub>2</sub>-Ar and measured for

the second time after reduction at 323 K. As shown in table 3, the initial CO-chemisorption capacity and the active metal surface area get reduced to about 30% of the values of the room temperature reduced sample, after being further reduced at 573 K. After re-calcination and subsequent reduction at 323 K the initial chemisorption capacity of the sample gets restored completely. A fresh batch of the sample has furthermore been reduced at 723 K in order to study the surface properties after the reduction peak in the TPR profile, shown in figure 1. Further reduction of the chemisorption capacity, compared to the measurement after 573 K treatment could be detected. Whereas the reduced uptake after reduction until 573 K could be ascribed to alloy formation, the decrease after 723 K reduction should be a result of the additional formation of a  $ZnO_x$  over-layer respectively Zn enrichment at the surface of the alloy, induced by SMSI.

The 5 wt.-% sample has also been studied by CO-chemisorption after different reductive pre-treatments, according to the TPR-profile shown in figure 1D. The dependence of the strong (chemisorption) adsorption isotherms of the reduction temperatures 323, 573 and 723 K is presented in supplemental part (Fig. S3). The adsorbed CO volume until saturation of the noble metal surface got reduced by 50% after the 573 K-reduction, which could be again explained by alloy formation. After 723 K-reduction, the CO-uptake has been further reduced, now by 75% compared to the original uptake after 323 K reduction.

Table 3: monolayer capacities in CO chemisorption and determined active metal surface area of the 2.5 % Pd/ZnO sample after reduction at 323 K, 623 K, recalcination and repeated 323 K-reduction and after 723 K-reduction (fresh sample)

reduction temperature (K)	monolayer capacity ( $\mu\text{mol/g}$ )	active metal surface area ( $\text{m}^2/\text{g}$ )
323	33.8	3.2
623	10.0	0.9
323 (rec.)	36.6	3.5
723	6.8	0.6

### 3.6 Summary

In the present study the electronic and structural constitution at the surface of variously loaded Pd/ZnO catalysts during reduction in different media and its influence on catalytic CO-oxidation was investigated. Homogeneously distributed Pd particles with narrow variation of BET surface area were obtained by controlled co-precipitation. We found that TPR in CO atmosphere was a more specific method to distinguish between different reduction steps, compared to hydrogen atmosphere. XRD measurements of the higher loaded samples showed that the bulk phase transformation into intermetallic PdZn happens to a major extent above 473 K, while beginning alloying at the surface starting already at this temperature in hydrogen atmosphere cannot be excluded. Further measurements confirmed that major PdZn formation takes place in case of reduction at 623 K in CO atmosphere. All CO-TPR profiles showed two pronounced reduction signals above PdO reduction

temperature, while their intensity ratio depended on the sample loading. Catalytic measurements were able to confirm a reversible process happening at the surface during reduction and being beneficial for CO-oxidation activity. This was basically independent of the reduction atmosphere, reduction temperature and catalyst loading, probably due to a similar energy density at the Fermi edge, irrespective of the actual chemical species present.

The low loaded sample reduced in CO below 423 K however became more active during the reaction cycles which might be an indication for not completely reduced palladium species in that case or beginning surface changes. When being reduced after the first TPR signal (523 K) the activity during the first reaction cycle is remarkably higher than in the following cycles, when the catalyst returns to a deactivated state. When reduced at the highest temperature (623 K) the sample got deactivated in general, with the first cycle still being more active, but also with a less pronounced difference between the cycles. HR-TEM and DRIFTS studies in that case confirmed the formation of an SMSI induced  $\text{ZnO}_x$  over-layer, leading to a suppressed CO adsorption capacity and explaining the loss of activity compared to the 523 K reduction step, where IR measurements confirmed the formation of surface alloy. Shape and slope of the conversion curves are an indicator for the chemical dynamics and the distribution of active sites. Activation energy determined in deactivated state was found to vary between 49 (0.75% sample, CO reduction at 623 K) and 82 kJ/mol (2.5% sample,  $\text{H}_2$ -reduction at 723 K). In case of hydrogen reduction of the 2.5 wt.-% sample, XPS confirmed the electronic modification at the surface, induced by surface alloying at 473 K already as well as the reversibility of that process and the oxidative decomposition of the surface alloy after air contact as reported previously by Föttinger et al.[22]. This reversible process was also confirmed by CO-chemisorption measurements, by a reduced CO adsorption capacity after reduction and a restoration during re-calcination and RT-reduction. Furthermore these measurements confirmed the trend of loss of active surface area with increasing reduction temperature.

#### 4. Conclusion

Electronic and structural surface modifications like alloying and  $\text{ZnO}_x$  over-layer formation both take place during the performed reduction treatments of the Pd/ZnO catalysts and cannot be clearly separated. Though both processes can be explained by the presence of strong metal-support interaction, the original idea of SMSI just described the over-growth of the noble metal by a reduced oxidic support without discussing alloying before or afterwards. The order of the described processes during TPR might also be dependent on the palladium loading, but according to our results there is a tendency of the occurrence of electronic surface modifications (alloying), increasing the CO-oxidation activity before additional SMSI-induced over-growth by a  $\text{ZnO}_x$  layer decreasing the CO-oxidation activity due to a loss of accessible active sites.

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## Figure Captions:

Fig. 1: TPR studies of the 2.5 (A,C) and 5 wt.-% (B,D) sample using CO (A,B) or H<sub>2</sub> (C,D) gas mixtures as reducing agent. The dashed black line intersecting the ordinate at zero is a guide to the eye.

Fig. 2: Rietveld refined XRD measurements after reduction in 2% CO of the 2.5 wt.-% sample (reduction temperature 473 K, part A) and of the 5 wt.-% sample (reduction temperature 623 K, part B).

Fig. 3: CO-oxidation (conversion cycles) of 0.75% Pd/ZnO sample after reduction in 2% CO-He at 423 K (1), 523 K (2, repeated measurement) and 623 K (3) and activation energy determined after the last measurement. Corresponding TPR-experiment presented in first row (left).

Fig. 4: CO-oxidation cycles of the 2.5% Pd/ZnO sample after repeated reduction in 5% H<sub>2</sub> at 473 K (A,B), at 573 K (new sample, C) and at 723 K (new sample, D, with determination of activation energy in the deactivated state afterwards, E) and comparison to measurement after reduction in 2% CO at 473 K (F).

Fig. 5: 0.75 wt.-% Pd/ZnO sample: SEM-image in calcined state (colored yellow, a), HAADF-STEM image after reduction in hydrogen at 323 K (Pd in red frame colored blue, b), HR-TEM images after reduction in 5% CO/Ar at 623 K at different focus (c-e) and proposed schematics for the catalyst state after 623 K-reduction (PdZn colored purple, ZnO<sub>x</sub> overlayer colored green, f). Original image presented in SI (Fig. S5).

Fig. 6: DRIFTS measurement of 0.75% Pd/ZnO sample during decreasing CO-partial pressure at 77 K, after reduction for 30 min in 2% CO-Ar at 323 K (A), 523 K (B) and 623 K (C).

Fig. 7: Zn segregation at the surface relative to the bulk composition during reduction of sample # 16688.

Fig. 8: Comparison of Pd3d<sub>5/2</sub> composition at different conditions ( $E_{kin} = 200$  eV). Pre-reduced 2.5% sample (16949, center) and deactivated sample (16957) after CO-oxidation (lower layer) and after successive in-situ reduction process in XPS-setup (top layer).