

Formation and catalytic activity of partially oxidized Pd nanoparticles

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Combining multi molecular beam (MB) experiments and in-situ time-resolved infrared reflection absorption spectroscopy (TR-IRAS), we have studied the formation and catalytic activity of Pd oxide species on a well-defined Fe₃O₄ supported Pd model catalyst. It was found that for oxidation temperatures up to 450 K oxygen predominantly chemisorbs on metallic Pd whereas at 500 K and above ($\sim 10^{-6}$ mbar effective oxygen pressure) large amounts of Pd oxide are formed. These Pd oxide species preferentially form a thin layer at the particle/support interface. Their formation and reduction is fully reversible. As a consequence, the Pd interface oxide layer acts as an oxygen reservoir providing oxygen for catalytic surface reactions. In addition to the Pd interface oxide, the formation of surface oxides was also observed for temperatures above 500 K. The extent of surface oxide formation critically depends on the oxidation temperature resulting in partially oxidized Pd particles between 500 and 600 K. It is shown that the catalytic activity of the model catalyst for CO oxidation decreases significantly with increasing surface oxide coverage independent of the composition of the reactants. We address this deactivation of the catalyst to the weak CO adsorption on Pd surface oxides, leading to a very low reaction probability.

KEY WORDS: model catalysts; surface reaction kinetics; molecular beams; surface oxidation; palladium; iron oxide; CO oxidation.

1. Introduction

Oxide supported metal nanoparticles are commonly used as catalysts for oxidation reactions in chemical industry, emission control and energy technology [1, 2]. Often, it is found that the activity and selectivity of such supported catalysts are critically controlled by the surface structure and morphology of the active metal particles as well as by the interactions between the metal particles and the oxide support. Consequently, the catalyst's activity may be very sensitive to structural changes at the microscopic level. In particular on transition metal surfaces in oxygen containing environments, major structural changes may occur, connected to the formation of different oxide species, e.g. chemisorbed oxygen (i.e. oxygen adsorbed above the first atomic layer of the metal), surface oxides (i.e. two-dimensional structures consisting of oxygen and metal layers) or bulk metal oxides (see e.g. [3–12] and references therein). It has been shown that the formation of such surface oxides is associated with significant changes in the catalytic activity of single crystal surfaces [13–15]. However, in most cases the role of the various oxygen species in the kinetics of surface reactions is not well understood.

In order to correlate the activity of supported Pd catalysts with the formation of different oxygen species on a microscopic level, we have combined two experimental approaches: First we employ well-defined

model catalyst surfaces. The use of model catalysts is motivated by the vast structural complexity of real heterogeneous catalysts and their limited accessibility to surface science techniques. Both points often preclude detailed insights into the surface chemistry and structure of real catalysts. Supported model catalysts, in contrast, provide clean, well-defined surfaces with strongly reduced complexity, which can be easily characterized at the atomic level (see e.g. [16–20] for recent reviews on model catalysts). Secondly, we probe the formation and activity of the different oxygen species on the model catalyst by multi molecular beam (MB) experiments under extremely well-defined reaction conditions. Simultaneously, the catalyst surface is characterized by in-situ time-resolved infrared reflection absorption spectroscopy (TR-IRAS). This approach enables us to obtain detailed information on the catalytic activity and structure of the catalyst.

Recently, we have studied the formation and activity of different oxygen species on a Pd/Fe₃O₄ model catalyst over a broad range of temperatures [21–25]: For oxidation temperatures up to 450 K oxygen was found to primarily chemisorb dissociatively on metallic Pd surface areas. At temperatures at 500 K and above, however, Pd oxide species are formed. Oxide formation initially occurs at the particle/support interface and, at a later stage, also on the outer particle surface [21, 24]. The Pd oxidation is strongly particle size dependent. While small Pd particles (<3 nm) can be almost completely oxidized to PdO by oxidation at 500 K, the oxide formation on larger Pd particles (>10 nm) is significantly reduced by kinetic hindrances due to a

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limited amount of accessible interface sites which facilitate the oxidation process [23]. In this contribution we show that the formation and reduction of Pd oxides is fully reversible. Therefore Pd interface oxide species act as an oxygen reservoir for catalytic surface reactions. Additionally, we discuss the catalytic activity of the different oxygen species for CO oxidation under steady state reaction conditions.

2. Experimental

All experiments were performed in an ultrahigh vacuum (UHV) apparatus at the Fritz-Haber-Institut (Berlin), which has recently been described [26]. The system offers the experimental possibility of crossing up to three beams on the sample surface. A schematic representation of the setup is shown in figure 1(a). The effusive beams were generated by doubly differentially pumped sources based on multi-channel arrays. Typical beam intensities were between 1.1×10^{13} and 2.2×10^{14} molecules $\text{cm}^{-2}\text{s}^{-1}$. The supersonic beam was generated by a triply differentially pumped source from a supersonic expansion. The beam intensity was 4.6×10^{14} molecules $\text{cm}^{-2}\text{s}^{-1}$. All experiments have been performed using $^{18}\text{O}_2$ (Campro Scientific, 95% ^{18}O , 99.7% purity), $^{16}\text{O}_2$ (Linde, 99,999%) and C^{16}O (Linde, 99,997% further purified by a gas filter (Mykrolis)). For gas-phase detection an automated QMS system (ABB Extrel) was employed. IRAS spectra were acquired by a vacuum FT-IR spectrometer (Bruker IFS 66v) with a spectral resolution of 2 cm^{-1} , using an MIR polarizer to select the p-component of the IR light only.

The model catalyst was prepared by deposition of a thin ($\sim 100 \text{ \AA}$), well-ordered Fe_3O_4 film on Pt(111) (see

[27, 28] for details). Subsequently Pd particles ($> 99.9\%$, Goodfellow) were grown on the Fe_3O_4 film by physical vapor deposition (Pd coverage: 2.7×10^{15} atoms cm^{-2} , sample temperature: 115 K) using a commercial evaporator (Focus, EFM 3). Directly after Pd deposition, the sample was annealed to 600 K and stabilized by oxidation and reduction at 500 K to form well-shaped and crystalline particles. Growth, structure and adsorption properties of the Pd particles have been studied in detail, recently [22]. An STM image of the stabilized model catalyst surface is shown in figure 1(b).

3. Results and discussion

In order to quantitatively study the formation of oxygen species on the Pd/ Fe_3O_4 model catalyst, we have determined the oxygen uptake and release of the model catalyst by pulsed MB titration experiments at different surface temperatures (figure 2): First the sample was exposed to a pulse of oxygen (1.7×10^{-6} mbar for 100 s). After a short delay time (10 s), 240 pulses of CO (5 s on-time, 5 s off-time, 8×10^{-7} mbar) were applied to probe the oxygen release by CO oxidation to CO_2 , which desorbs immediately and can be detected in the gas-phase. In figure 2(a), the CO_2 formation rate of such a pulsed MB titration experiment at 500 K is shown. Here, the reaction rate is fast for the very first CO pulse but still finite for up to 100 following pulses. By integrating the CO_2 formation over all CO pulses applied, the total amount of oxygen withdrawn out of the sample can easily be estimated from this experiment. The integral oxygen release at different surface temperatures is shown in figure 2(b). Interestingly, the total oxygen storage capacity of the model catalyst at 500 K is nearly

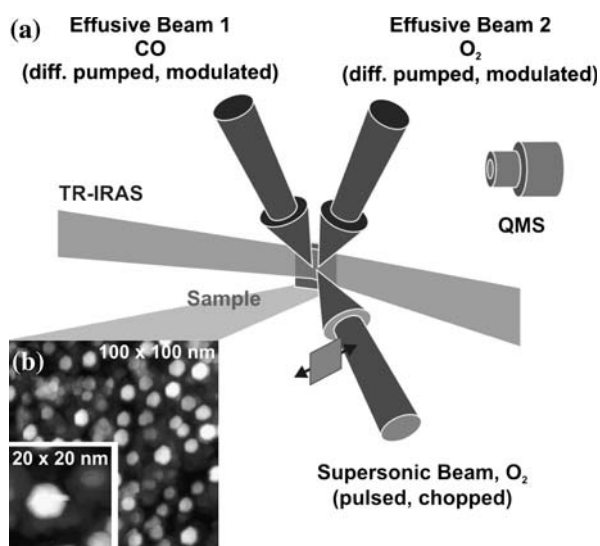


Figure 1. (a) Schematic representation of the molecular beam setup; (b) STM image ($100 \text{ nm} \times 100 \text{ nm}$, inset $20 \times 20 \text{ nm}$) of the Pd model catalyst.

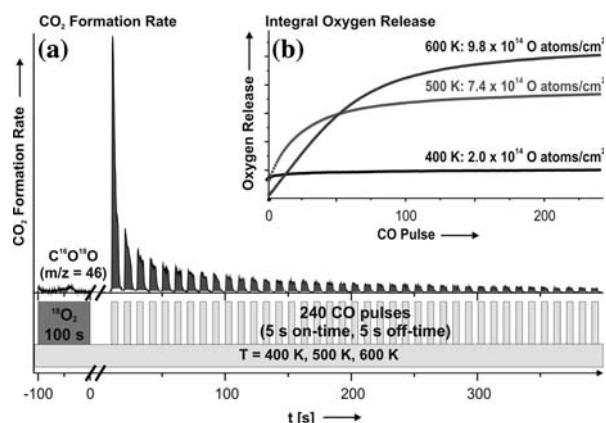


Figure 2. Pulsed CO titration experiment on the Pd/ Fe_3O_4 model catalyst after oxygen exposure at different surface temperatures: First the sample is exposed to an oxygen pulse (1.7×10^{-6} mbar, 100 s). Subsequently 240 CO pulses (5s on-time (8×10^{-7} mbar), 5 s off-time) are applied to withdraw oxygen stored in the catalyst in form of CO_2 ; (a) CO_2 formation rate for a surface temperature of 500 K; (b) Integral oxygen release for different surface temperatures.

4 times and at 600 K nearly 5 times higher compared to the amount of oxygen stored at 400 K.

In Pd single crystal studies it has previously been shown that up to 400 K oxygen mainly adsorbs dissociatively forming an ordered overlayer of chemisorbed oxygen [3, 4]. For oxidation temperatures above 500 K, however, the formation of surface oxides has been reported for various Pd single crystal surface (see e.g. [9, 10] and references therein). These surface oxides involve major reconstructions of the Pd surface and their oxygen density ($\theta \sim 1$, see e.g. [8, 9]) exceeds by far the density of chemisorbed oxygen overlayers.

In view of the above, we explain the large oxygen uptake above 500 K by the formation of Pd oxide species while the amount of oxygen stored at 400 K is assigned to chemisorbed oxygen only. Recently we have shown that these Pd oxide species are preferentially formed at the particle/support interface [21]. As a consequence, despite the large Pd oxide formation after oxidation at 500 K the outer particle surface remains mainly metallic. To quantify the oxygen storage capacity, the amount of Pd surface atoms was determined on the basis of CO adsorption experiments as 6.0×10^{14} atoms cm^{-2} . Assuming an oxygen coverage of $\theta \sim 0.30$ for chemisorbed oxygen on Pd particles (80% Pd(111): $\theta = 0.25$ [3]; 20% Pd(100): $\theta = 0.50$ [4]) we estimate the oxygen storage capacity of the model catalyst to be 2.0×10^{14} atoms cm^{-2} after oxidation at 400 K (see [24] for details). Accordingly, the oxygen storage capacity at 500 K amounts to 7.4×10^{14} atoms cm^{-2} but can be

further increased up to 1.6×10^{15} atoms cm^{-2} by extending the oxygen exposure [24]. However, a complete oxidation of the Pd particles cannot be obtained even after extended oxygen exposure under the conditions applied in this work. The CO titration experiments show that the oxidation and reduction of the Pd particles is a fully reversible process. As a result the Pd interface oxide layer acts as a reservoir, which can accumulate oxygen under oxidizing conditions and subsequently provide oxygen for surface reactions under reducing conditions. Apart from Pd oxide formation, an additional oxygen storage channel based on oxygen migration from the particles onto and into the support (oxygen spillover) could be invoked. However, titration experiments on isotopically labeled supports show that oxygen exchange with the support is negligible under the experimental conditions applied in this work [24].

In addition to the Pd interface oxide, Pd surface oxides can also be formed at oxidation temperatures above 500 K [22, 24]. It was found that with increasing oxidation temperatures an increasing fraction of the Pd surface becomes oxidized resulting in a partially oxidized Pd surface for oxidation temperatures between 500 and 600 K. To study the influence of these Pd surface oxides on the kinetics of CO oxidation under steady-state conditions, combined MB/TR-IRAS experiments have been performed on pre-oxidized Pd particles. The exposure and temperature sequence of the experiments is schematically shown in figure 3(a): First the sample was exposed to oxygen (8×10^{-7} mbar for 1,000 s) at

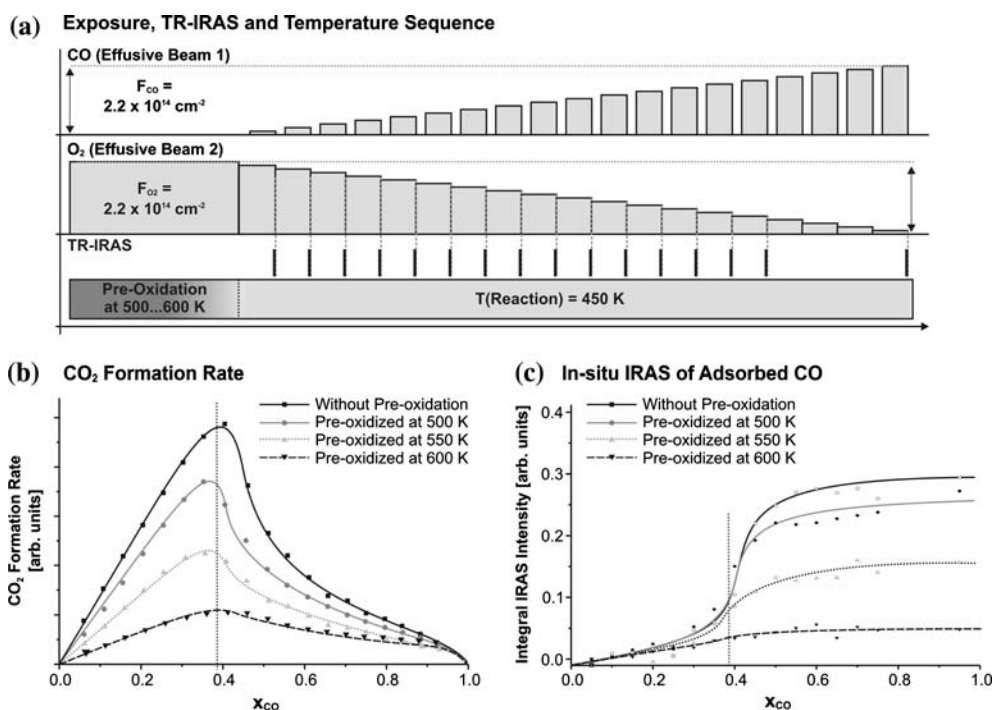


Figure 3. CO oxidation on partially oxidized Pd/Fe₃O₄ model catalysts at 450 K: (a) Exposure, TR-IRAS and temperature sequence of the experiments; (b) Steady state CO₂ formation rate and (c) integral IRAS intensity in the CO stretching frequency region as a function of CO and O₂ flux at a surface temperature of 450 K.

different temperatures (500–600 K) leading to a partial oxidation of the particle surface. This procedure is referred to as “pre-oxidation” in the following. Subsequently the sample was cooled to the reaction temperature (450 K) in oxygen. Finally, the reaction kinetics on the model catalyst were studied as a function of CO/O₂ ratio. For each CO/O₂ ratio, the sample was first exposed to oxygen only (formation of an oxygen saturated surface) and, thereafter, to both reactants at a given x_{CO} . After steady-state conditions were established, the CO₂ formation rate was determined by means of the QMS and IRAS spectra were acquired under reaction conditions. Additionally, a reference experiment without pre-oxidation was performed to study the CO₂ formation rate on the reduced model catalyst.

The steady state CO₂ formation rate as a function of the composition of the reactants is shown in figure 3(b). The qualitative behavior is relatively similar independent of the pre-oxidation temperature: In any case, under O-rich conditions ($x_{\text{CO}} < 0.4$) the reaction rate scales almost linear with the CO partial pressure. At the transition point between the O-rich and the CO-rich region at $x_{\text{CO}} \sim 0.4$, the CO₂ formation rate decreases significantly resulting in a lower reaction rate under CO-rich conditions ($x_{\text{CO}} > 0.4$). For a detailed discussion of the steady state behavior we refer to the literature [20, 29]. Quantitatively, however, the CO₂ formation rate on the pre-oxidized samples decreases drastically with increasing pre-oxidation temperature. After pre-oxidation at 600 K the reaction rate is $\sim 70\%$ lower with respect to the reduced sample. The IRAS intensity in the CO stretching frequency region as a function of CO/O₂-ratio is shown in figure 3(c): In all cases almost no CO coverage was found under O-rich conditions ($x_{\text{CO}} < 0.4$), while a nearly constant CO coverage under CO-rich conditions ($x_{\text{CO}} > 0.4$) was observed. The IRAS intensity of adsorbed CO on the pre-oxidized samples, however, is significantly lower compared to the reduced surface (figure 3(c)). It should be noted that IRAS intensities do not directly reflect the CO coverage due to dipole coupling effects [30]. Still, it is apparent that the total CO coverage decreases with increasing pre-oxidation temperature, which can be related to the weak adsorption of CO on oxidized Pd (compare [24]).

The IRAS data obtained under reaction conditions directly reflects the oxidation behavior of the Pd/Fe₃O₄ model catalyst as recently studied [21, 22, 24]. It was found that with rising oxidation temperatures an increasing fraction of the Pd particle surface becomes covered by surface oxides. The formation of such Pd surface oxides, however, significantly modifies the adsorption properties of the model catalyst, i.e. significantly lowering its CO and oxygen adsorption capacity.

In view of these results, two main conclusions can be drawn from the experiments shown in figure 3: most important to note is the reduced CO₂ formation rate

with increasing pre-oxidation temperature. It is apparent that the lower catalytic activity of the pre-oxidized samples is related to the formation of surface oxides. The IRAS results show that there is essentially no CO adsorption on the oxidized Pd surface. Hence, it appears likely that the CO oxidation occurs mainly on metallic Pd surface areas involving chemisorbed oxygen. This conclusion is in line with recent CO titration experiments, which have also indicated a negligible activity of Pd surface oxides for CO oxidation [21]. Secondly, it is noteworthy to point out that the reaction rate on the pre-oxidized system is lower than on the non-oxidized sample even under CO-rich conditions, where dissociative oxygen adsorption is the rate limiting step of the reaction. Here, an additional oxygen supply by decomposition of Pd oxides enhancing the CO₂ formation on the catalyst surface could be invoked. However, even after extended exposure to the reactants at 450 K under CO-rich conditions, no significant increase of the CO coverage can be observed in IRAS, which would indicate a reduction of the Pd surface on the pre-oxidized sample (figure 3(c)). Therefore, we presume the reduction of Pd oxide species by CO to be kinetically hindered at 450 K. As a consequence, the formation of Pd surface oxide species at higher oxidation temperatures causes a deactivation of the catalyst at lower reactions temperatures independent of the composition of the reactants. For a more detailed discussion of the CO oxidation kinetics on partially oxidized Pd particles in a broad temperature range we refer to the literature [25].

4. Conclusions

In this contribution we have studied the formation of Pd oxide species on Fe₃O₄ supported Pd catalysts and the activity of these different oxygen species for CO oxidation by multi molecular beam and TR-IRAS experiments on well-defined model catalyst surfaces:

- (i) *Oxygen Storage at particle/support interface*: For oxidation temperatures above 500 K large amounts of oxygen can be stored in the model catalyst in form of a thin Pd oxide layer at the particle/support interface. This oxygen reservoir can be reversibly accumulated and depleted providing oxygen for catalytic surface reactions. It may be anticipated that similar storage mechanisms might be active for other dispersed metal catalysts on reducible or irreducible oxide supports as well.
- (ii) *Catalyst deactivation by Pd surface oxidation*: The formation of Pd surface oxides at higher oxidation temperatures ($T > 500$ K) drastically lowers the activity of the model catalyst at lower reaction temperatures ($T < 450$ K). Therefore we assume that CO oxidation occurs mainly on metallic Pd surface areas, whereas the reaction probability for CO oxidation on Pd surface oxides is drastically lower.

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