Adsorbate-induced restructuring and pressure-dependent adsorption on metal nanoparticles studied by electron microscopy and sum frequency generation spectroscopy

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Dedicated to Gabor A. Somorjai on the occasion of his 65th birthday

Several examples are presented that illustrate how the internal and surface structure of oxide supported Pt nanoparticles can change under reaction conditions. High temperatures and the presence of adsorbates may lead to different effects: (1) changes in the particle size distribution (sintering or redispersion) that may affect the crystallographic and electronic structure of the nanoparticles, (2) restructuring of the particle surface facets, and (3) crystallization of large polycrystalline aggregates. Three different model systems are described that are well-suited for high resolution transmission electron microscopy (HRTEM) and/or surface science techniques. To examine the influence of high gas pressure on the structure of adsorbates, infrared-visible sum frequency generation (SFG) surface vibrational spectroscopy is applied to monitor CO adsorption on supported Pd nanoparticles from 10^{-7} to 200 mbar. The adsorption site occupancy of CO, in particular the on-top population, strongly depends on pressure and temperature preventing a simple extrapolation of low pressure results to reaction conditions.

KEY WORDS: platinum; palladium; alumina; silica; nanoparticles; electron microscopy; sum frequency generation; carbon monoxide; adsorption; vibrational spectroscopy; high pressure

1. Introduction

Many important concepts in heterogeneous catalysis, such as the particle size effect, metal-support interaction, the influence of various promoters and poisons, etc. were already recognized several decades ago (e.g., [1-6]). These effects were identified based on the observation of the activity and selectivity of different supported catalysts but a detailed investigation of their molecular origin was not possible, due to the complex structure and composition of high surface area catalysts. Consequently, catalysis was long considered rather an "art" than a thorough scientific approach. In the 1960s, this situation was drastically changed by the introduction of affordable ultrahigh vacuum (UHV) systems and the development of a variety of surface sensitive techniques [7-9]. Clean single crystal surfaces and their interaction with gas molecules could be studied on an atomic scale providing information on various surface and adsorbate properties, including structure, composition, oxidation states, etc.

Gabor Somorjai is one of the pioneers of applying molecular surface chemistry to study catalytic phenomena. The importance of the relaxation and reconstruction of clean surfaces, of adsorbate-induced restructuring and of defect sites was demonstrated with significant impact from the Berkeley laboratory [10,11]. When high pressure cells were attached to a UHV surface analysis apparatus [12–14], a single crystal could be tested in a catalytic reaction at atmospheric pressure, with pre- and post-reaction surface analysis in UHV.

Very soon structure sensitivity could be studied by utilizing single crystal surfaces of various orientations [15-17] and metal-support interaction was tackled by depositing oxide overlayers on metal surfaces [18,19]. These studies also revealed that the structure and composition of a catalyst is often changed during the reaction [20,21] which was later corroborated by scanning tunneling microscopy (STM) [22,23]. Furthermore, the high gas pressure involved in a catalytic reaction may lead to surface coverages and, hence, structures of adsorbates that cannot be obtained at the fairly low exposures generally applied in UHV studies (around 10^{-6} mbar) [24]. If the nature of an adsorbate depends on pressure, a simple extrapolation of UHV results to reaction conditions is not possible. These considerations illustrate the need of in situ characterization, and a few in situ high pressure surface sensitive techniques are available today [8,25,26].

Single crystal surfaces of various orientations may be chosen as model catalysts and they can be even modified by (oxide, metal, etc.) deposits, but it is obvious that this approach is unable to fully model the complex structure of a supported catalyst. For instance, the diffusion-coupled interplay between the different facets of a nanoparticle [27] or the size-dependent electronic structure of a metal nanoparticle cannot be represented by a cm-size single crystal [28]. In order to tackle this problem, well-defined model systems for supported catalysts were developed, that can still be studied by most surface science techniques. These model catalysts often consist of metal deposits on flat supports and are generally prepared in ultrahigh vacuum (for reviews see [29–33]).

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In this communication we present several case studies from our previous work that show how reaction conditions, i.e., high pressures (a few hundred mbar) and/or high temperatures, can influence the internal and surface structure of metal nanoparticles, and how the adsorption site distribution of CO molecules on metal aggregates depends on pressure. To examine surface structural changes we will employ transmission electron microscopy (TEM), in part carried out *in situ*, while the pressure-dependent adsorbate structure of CO will be examined by *in situ* laser spectroscopy (sum frequency generation; SFG). The results show that both the catalytic surface as well as the adsorbate are dynamic under reactions conditions, in agreement with the concept of a *flexible surface* [8,19,20].

2. Experimental

Three different types of model catalysts were utilized that allow the application of electron microscopy and/or surface science probes including laser spectroscopy. Details about the preparation procedures can be found in previous publications [30,34-38] and only a brief summary is given here. The first and second route produce small and homogeneously distributed metal nanoparticles but only with limited control of interparticle distances. The third route allows to precisely control the position and spacing of the metal particles but is currently limited to particle sizes >10 nm.

2.1. Pt particles grown on an ordered Al₂O₃ film on NiAl(110) [30,38]

A NiAl(110) single crystal substrate was used to grow a thin (~ 0.5 nm) ordered aluminum oxide film by oxidation in 10^{-5} mbar O₂ at 523 K (for details concerning the film structure see [30]). Pt was subsequently deposited onto the alumina support at 300 K by electron beam evaporation of a Pt wire (rate of 0.2 nm min⁻¹). By accurately controlling the substrate temperature and the amount of metal deposited, the cluster size and number density can be adjusted, producing mean particle sizes ranging from only a few atoms to several ten thousand atoms per particle [30,38]. Pd/Al₂O₃ catalysts were produced following the same procedure. Due to the very small thickness of the supporting oxide this type of model catalyst allows to utilize methods which rely on a good electrical or thermal conductivity such as scanning tunneling microscopy (STM), low energy electron diffraction (LEED) or temperature programmed desorption (TPD). In addition, the "flatness" of the supporting film facilitates laser spectroscopy, as will be described in section 4. To make this model catalyst compatible with electron microscopy, a prethinned (ion-milled) NiAl(110) crystal was used as substrate that had an electron transparent window in the center (figure 1(a)) [39].

2.2. Epitaxially grown Pt nanocrystals supported on Al₂O₃ [34,35]

The preparation of this metal/oxide system was also performed in two steps, however, in the reverse order: First, Pt nanocrystals were grown epitaxially on NaCl(100) by vacuum deposition at a substrate temperature of 593 K. Pt was evaporated by electron beam bombardment of a 1 mm \varnothing Pt wire at a flux of 5×10^{13} atoms cm⁻² s⁻¹ up to a nominal film thickness of 0.8 nm. In the second step, the Pt nanoparticles were embedded at room temperature in a thin amorphous Al₂O₃ film by evaporation of Al in 10^{-4} mbar O₂ $(1 \text{ nm} \text{min}^{-1}; \text{ thickness } 25 \text{ nm})$. The resulting metal/oxide films were removed from the NaCl substrate by flotation, rinsed in water and mounted on gold grids for electron microscopy examination. Using the same procedure, a variety of metal-oxide combinations can be obtained [34,40]. Microreactor kinetic measurements on this type of model catalyst are reported elsewhere [41].

2.3. Pt nanoparticle arrays on SiO₂/Si(100) [36,37]

Pt nanoparticle arrays with well-defined particle size and spacing were produced by electron beam lithography (EBL). The EBL fabrication process consists of several steps (a scheme is shown in [31,36]). First, a 5 nm thick amorphous silica support was prepared on a Si(100) wafer by surface oxidation [42]. The next step is to spin-coat an 80 nm thick electron-sensitive polymer (polymethylmethacrylate, PMMA) onto the support surface. The desired pattern is then "written" into the polymer layer by a highly collimated electron beam (Ø 4 nm, 100 kV, "nanowriter" by Leica Corp.). This is followed by the selective dissolution of the polymer areas damaged by the electron beam in a methylisobutyl ketone/isopropyl alcohol mixture. This procedure produces a mask of periodically-spaced holes in the PMMA layer. A thin film of metal (15 nm) is then evaporated onto this mask and after the remaining polymer resist is removed completely by dissolution in acetone, metal nanoparticles of the prescribed pattern remain on the support. For electron microscopy examination, the samples were thinned from the back to form an electron transparent window (similar to figure 1(a)). Al₂O₃ supported catalysts can be prepared by deposition of a thin alumina film onto the Si substrate prior to the metal evaporation [37].

2.4. Characterization techniques

Several electron microscopy techniques were utilized to determine the shape and the microstructure of the model catalysts [43–45]: Conventional transmission electron microscopy (TEM), selected area electron diffraction (SAED), weak beam dark field (WBDF) imaging [Zeiss EM 10C and Jeol 100C operated at 100 kV] and high resolution transmission electron microsopy (HRTEM) [Jeol ARM 1000 operated at 800 kV, Jeol 4000 EX operated at 400 kV and Hitachi 8100 at 200 kV]. WBDF imaging allows to

Pt ($\bar{d} = 2 \text{ nm}$)/Al₂O₃/NiAl(110)



Figure 1. (a) Schematic cross section of the ion-milled NiAl(110) substrate crystal; (b) side view of the oxidized wedge; (c) transmission electron micrograph of a Pt/Al₂O₃/NiAl(110) model catalyst; (d) high resolution image of supported Pt clusters; the inset shows an expanded view of the marked particle (2.87 Å is the lattice spacing of (001) planes of NiAl, a_M indicates the Moiré periodicity); (e) lattice constant and interatomic distance of Pt particles vs. particle size (horizontal bars represent the width and length of the clusters, vertical bars are error bars).

determine the shape of nanocrystals and to identify different domains in polycrystalline aggregates (for details

see [33,35,43]). To determine lattice spacings and angles between atomic planes fast Fourier transforms (FFTs)

of digitized HRTEM images of individual particles were used.

A brief discussion of the SFG process can be found in section 4. To acquire an SFG vibrational spectrum of adsorbate molecules on a catalyst surface, two picosecondlaserpulses are spatially and temporally overlapped on the sample. One input beam is in the visible range at fixed frequency (ω_{vis}), while the second one is tunable in the infrared $(\omega_{\rm IR})$. When the IR beam is tuned through a vibrational resonance of the adsorbate, a photon at the sum of the two input photon frequencies ($\omega_{\text{SFG}} = \omega_{\text{vis}} + \omega_{\text{IR}}$) is emitted. The SFG signal is monitored by a detection system (including filters, a monochromator and a photomultiplier) and plotted vs. the IR energy. The visible radiation for the experiment (790 nm, 2 mJ/pulse, 2 ps, 500 Hz) is generated by an amplified titanium sapphire laser, and 90% of its output is used to generate tunable infrared light (3–6 μ m, ca. 10 μ J/pulse) with an optical parametric generator/amplifier (OPG/OPA).

The setup for *in situ* sum frequency spectroscopy has been presented in detail elsewhere and will be only briefly described here [13]. The experiments were performed in a custom-designed apparatus that combines a UHV surface analysis chamber and an SFG-compatible UHV-high pressure reaction cell. Supported nanoparticles are prepared and characterized under well-controlled conditions in UHV, with subsequent UHV-transfer to the SFG cell. The SFG cell is equipped with two CaF2 windows and allows one to monitor adsorbates from submonolayer coverages up to several 100 mbar by SFG spectroscopy. Although the SFG cell was designed to minimize the IR path length between the sample and the input window (<5 cm), the absorption of the IR beam by gas phase CO at high pressure must be accounted for because the SFG signal intensity depends on the IR intensity. To compensate for the pressure-dependent attenuation of the IR beam and to normalize our SFG spectra, the energy-dependent IR absorption was determined using a GaAs reference crystal. All high pressure SFG spectra were corrected for gas phase absorption.

3. Electron microscopy studies of metal nanoparticles in different atmospheres

In the following we will describe how structural changes of metal nanoparticles under reaction conditions can affect the catalytic properties. We will distinguish three different cases, although they cannot be fully separated in reality: (1) Changes in the metal particle size (e.g., by sintering or redispersion), (2) surface structural changes of individual particles (without changes in particle size), and (3) crystallization of large polycrystalline aggregates by intraparticle metal diffusion. The effects are studied using three different model systems (cf. 2.1–2.3) that were utilized to produce metal aggregates over a wide size range (1–30 nm mean size).

Pt nanoparticles grown on $Al_2O_3/NiAl(110)$ (preparation 2.1) were applied in a TEM study of the effect of decreasing particle size on the crystal structure of metal aggregates [46].

As already mentioned, the NiAl(110) crystal was thinned to obtain a wedged hole in the center prior to oxidation (figure 1(a)). Resulting from this procedure an Al₂O₃ film supported by NiAl (darker areas in figure 1(c)) as well as unsupported Al₂O₃ (protruding over the NiAl edge; lighter regions in figure 1(c)) were obtained and used as substrate for subsequent metal deposition (figure 1(b)). Since no difference between metal particles grown on the supported and unsupported alumina was observed, in the following we will not differentiate between the two situations. Preceding studies had shown that air exposure during sample transport to the microscope had almost no influence on the supporting oxide and metal deposits [39,46].

Figure 1(c) shows an electron micrograph of a $Pt/Al_2O_3/$ NiAl(110) model catalyst with a mean Pt particle diameter of 2 nm. The same particle size distribution was observed with STM under UHV conditions [47]. In the HRTEM image of figure 1(d) some clusters show Moiré fringes that originate from double diffraction between the Pt lattice and the (crystalline) NiAl substrate. By careful analysis of the periodicity of the Moiré patterns [39], the Pt lattice constant was calculated as a function of particle size. The result is plotted in figure 1(e) and indicates a decrease of the lattice parameter with decreasing particle size. Pt clusters of ~ 1 nm size have a lattice constant that is only 90% of the bulk value while the bulk structure is observed for Pt particles ≥ 3 nm. This result was corroborated by transmission electron diffraction (SAED) [46]. A lattice contraction has also been observed for very small Pd particles but in this case only a 5% reduction was measured [48].

Lattice contractions of metal particles, which are often explained by surface stress inducing pressure inside the cluster [33], are generally observed only for very small sizes, i.e., $\leq 2-3$ nm. This deviation from the bulk crystallographic structure may be paralleled by a size-dependent electronic structure of nanoparticles [49,50] including a insulatormetal transition [28,29,51]. Furthermore, as suggested more than three decades ago by van Hardeveld et al. [3], the relative ratio of corner, edge and terrace sites on metal aggregates significantly changes in the size range between 1 and 5 nm for a variety of polyhedral shapes. These considerations illustrate that the "geometric" structure (internal and surface structure) and the electronic structure of metal nanoparticles may drastically change in the same size regime where structure sensitive reactions often exhibit the strongest variation in catalytic activity [29]. The close correlation between structure and catalytic performance is therefore apparent and may explain why very small Pt aggregates have remarkable chemical properties (e.g., the ability to dissociate CO [50]). Consequently, structure-activity correlations were frequently studied by monitoring the initial activity and selectivity of catalysts of different metal dispersion (particle size effect [6]). However, the metal particle size may change during the reaction, for instance, by sintering, with significant influence on the catalytic performance [52-56]. If the Pt particles on the unsupported alumina film (cf. figure 1(c)) were heated in UHV to 700 K, the cluster density decreased



Figure 2. (a) Electron micrograph of Pt nanocrystals on Al₂O₃; (b) HRTEM image of a cuboctahedral Pt particle (as-prepared); surface facets aligned parallel to the electron beam direction are indicated; (c) higher magnification of the top region of the particle shown in (b); the sketches show a half-octahedral particle (d), and a cuboctahedral particle in side-view (e) and in [110] zone axis orientation (f).

to about 50% while the mean particle size was nearly doubled [46].

However, even if the catalyst is stable enough to resist sintering, the presence of reactant gases may change the surface structure of the metal particles [23,57–63]. Upon thermal treatment the particles may undergo different morphological changes depending on the type of gas present (e.g., they may adopt equilibrium shapes, develop steps, break up, etc). Since the catalytic performance in structure-sensitive reactions critically depends on the nature of the surface sites present, surface structural changes resulting from gas exposure can also considerably influence the properties of a catalyst. Regeneration treatments make use of the same effect to reverse unfavorable structural changes and to regain active sites on the catalyst particles [35].

While sintering is rather easy to follow by TEM, atomic scale surface structural changes of *individual* metal particles are difficult to detect. Such a study requires regular shaped particles as well-defined starting point and, therefore, epitaxially grown Pt particles represent an ideal model. Using preparation procedure 2.2, homogeneous distributions of well-faceted polyhedral Pt nanocrystals were obtained (figure 2). Since the morphology and surface structure of the majority of the Pt particles are identical, surface structural changes can be detected without the need to examine the same Pt particle before and after a particular treatment. Figure 2(a) shows a plan-view image of Pt nanoparticles grown on NaCl(100) that were embedded in a thin amorphous Al₂O₃ film (the NaCl substrate was subsequently removed). The mean Pt particle size is 5 ± 1 nm with a particle number density of 7×10^{11} cm⁻². As result of the epitaxial growth, most Pt particles have square or rectangular outlines and their edges are parallel to each other. According to HRTEM and weak beam dark field (WBDF) imaging [34], most particles are single-crystalline half-octahedra (figure 2(d)) or rectangular pyramids with a (100) base plane and four {111} side faces. However, here we will direct our attention to Pt particles in [110] zone axis orientation, such as the one shown in figure 2(b), that are found in a smaller fraction (\sim 10%). Two families of {111} lattice fringes are

resolved in HRTEM images (figure 2(b)) and WBDF images prove that these particles have the shape of cuboctahedra, with small truncations at their base (figure 2(e)). Perfect cuboctahedra have only {111} and {100} surfaces but in the case of the particle in figure 2(b) the edge between two {111} facets is truncated by a {110} facet. The orientation of the cuboctahedra, with the surface facets along the perimeter aligned parallel to the electron beam (figure 2(f)), allows to record surface-profile images. For instance, in figure 2(b) we are "looking" parallel to the {111} facet on the top left side of the particle and we are thus able to recognize surface steps (while steps on facets that are inclined to the electron beam cannot be resolved; cf. figure 2(d)). During the growth process (metal evaporation) the number of Pt atoms per particle is continuously increased and consequently the surface facets are generally incomplete. Figure 2(c) shows a higher magnification of the top region of the cuboctahedron of figure 2(b) and a few monoatomic steps can be seen on the {100} and {111} surfaces. However, the number of steps is generally limited to one or two per facet. An extended study of HRTEM contrasts confirmed that epitaxially grown Pt cuboctahedra have smooth facets with a small number of surface steps and no kinks present [64]. The well-defined shape of these particles allows to follow surface structural changes induced, e.g., by oxidation-reduction treatments, similar to those that are often used to activate and rejuvenate supported metals.

Annealing the Pt particles in 1 bar O₂ at temperatures below 523 K had no effect on the particle shape but oxidation between 523 and 773 K led to a continuous rounding of the particle profiles indicating that steps and higher index facets were formed. Figure 3(a) shows a HRTEM micrograph of a Pt particle after oxidation at 673 K for 2 h. Most Pt particles have rounded outlines after this treatment, but this particular cuboctahedron has maintained some facets in its top region and illustrates the difference between a faceted and a rounded profile. A distinct {111} facet can still be recognized in the top part of the particle, while the rounded lower part of the particle can no longer be described by only {111}, {100} and {110} facets, indicating the presence of higher-index surfaces such as {311}, {331} etc. Figure 3(b) shows a higher magnification of the stepped surface at the lower left edge of the particle. Subsequent heat treatments in hydrogen up to 523 K did not change the particle surface structure and the stepped surfaces were maintained. Only after reduction in hydrogen around 723 K were the smooth low-index facets restored and the particles regained a well-faceted morphology (similar to figure 2(b)). Similar results were reported for impregnated (powder) catalysts [57,59,61]. A comprehensive discussion of possible driving forces for the observed structural changes, in terms of thermodynamic (surface energy changes upon adsorption) and kinetic arguments (growth shapes) were discussed in detail by Datye and coworkers [57].

The activation process described above comprises two effects: a thermal treatment and, simultaneously, the effect of gas adsorption. Annealing treatments in high vacuum are



Figure 3. (a) HRTEM micrograph of a Pt catalyst particle after oxidation at 673 K; (b) higher magnification view of the same particle showing several surface steps.

a way to differentiate between these two effects. Although modern high resolution electron microscopes are equipped with heating stages that allow *in situ* experiments, it is difficult to follow structural changes of metal nanoparticles during heat treatments because the thermal drift of the sample often prevents atomically resolved images. However, if the metal particles are big enough to allow the application of weak beam dark field microscopy this problem can be circumvented. Although WBDF imaging does not have atomic resolution, it can still provide valuable information about the crystallinity of metal particles [33,35].

Nanoparticle arrays fabricated by lithographic methods are well suited for such an experiment (preparation 2.3) and were mainly utilized by Wolf [42], Somorjai [36,65,66], Kasemo [67] and Prins [68]. Typical Pt particle sizes are around 20 nm and the small size distribution and the periodic arrangement of the metal particles facilitate the detection of particle mobility, sintering, etc. Furthermore, the variation of the particle separation allows a systematic study of reactions that are controlled by the diffusion of adsorbates be-



Figure 4. (a) Transmission electron micrograph of a Pt nanoparticle array on SiO₂/Si(100); (b) WBDF image of an individual Pt particle demonstrating its polycrystallinity; (c) electron diffraction pattern of the catalyst shown in (a); the Pt reflection used for dark field imaging is enhanced and marked by a circle.



Figure 5. Bright field and dark field micrographs of a Pt array on silica, taken *in situ* during annealing in high vacuum: (a,b) 773 K, (c,d) 973 K, (e,f) 1173 K.

tween the Pt particles. Figure 4(a) shows a bright field TEM micrograph of a Pt/SiO₂/Si(100) model catalyst with a mean particle size of 28 ± 3 nm, and an interparticle distance of 200 nm (resulting in 2.5×10^9 particles cm⁻²). An electron

diffraction pattern of this sample is shown in figure 4(c). It is dominated by reflections from the Si(100) substrate and only weak Pt spots are observed – one is enhanced and marked by a circle in figure 4(c). If this Pt reflection is used for



Figure 6. (a) HRTEM micrograph of a polycrystalline Pt particle (as-prepared); a crystallized Pt particle after annealing in vacuum to 1173 K is shown in (b); (c) higher magnification and FFT of the top right surface region of the particle in (b).

WBDF imaging (figures 4(b), 5(b)) the polycrystalline structure of the Pt clusters with domain sizes of about 5-8 nm is revealed. Of course, the different crystalline grains within one particle can be directly imaged by HRTEM (figure 6(a); Moiré fringes of 0.5 nm spacing are due to double diffraction of overlapping crystalline domains). The rounded profiles of the particles in TEM images suggest that their surfaces consists mainly of stepped high Miller-index facets.

The effect of annealing in vacuum (10^{-8} mbar) was studied by *in situ* electron microscopy. The Pt/SiO₂/Si(100) catalyst was heated up to 1173 K using a Gatan TEM heating holder (figure 5). Dark field microscopy (WBDF) allows one to monitor the internal structure of the Pt particles by monitoring the individual crystalline grains. The Pt array remained unchanged upon heating to 773 K for several hours and the particles maintained their polycrystalline structure (figures 5 (a) and (b)). Also, no changes were evident after heating to 873 K (1 h). After heating for 1 h to 973 K, the

dark field images showed that the crystalline domains of the particles grew in size and some of the particles fully crystallized and became single crystals (figures 5 (c) and (d)). The reduction of the number of grains per Pt particle is also evident from the reduced number of particles that are imaged in dark field. The metal crystallization continued until the final temperature of 1173 K was reached. Although the individual particles did not migrate over the support surface at any temperature, particle rounding and some new objects were observed after heating to 1173 K for 1 h (see arrows in figures 5 (e) and (f)). According to dark field microscopy, these features are small Pt aggregates that are probably formed by nucleation of Pt atoms migrating across the support at high temperature. The mobility of Pt at 1173 K also leads to a change in the particle size distribution to 23 ± 4 nm (figure 5(e)). At 973 K the Pt atom mobility seems to be restricted to intraparticle diffusion, since small aggregates were never observed between the Pt particles. To investigate

the possibility that Pt diffused across the silica surface even at 973 K, energy dispersive X-ray analysis (EDX) was performed in the TEM. Positioning an electron beam of 30 nm diameter close to a particle or at the spaces in between particles yielded no Pt emission. This does not fully rule out the possibility of Pt diffusing across the surface, but it renders significant Pt diffusion at 973 K unlikely. Figures 6 (b) and (c) show HRTEM images of a recrystallized Pt particle that exhibits distinct low Miller index surface facets, together with the corresponding fast Fourier transform (FFT) indicating a [110] zone axis orientation. Two driving forces can be considered for particle crystallization: (1) Pt diffusion within one particle, and (2) melting of the particles. Recently, Wang et al. observed surface melting on 8 nm Pt particles above 873 K (with the melting point depression due to the small radius of curvature of nanoparticle facets; [69] and references therein). However, the Pt particles in this study were much larger and no indication of surface melting was observed. Therefore, based on calculations of Pt selfdiffusion we favor intraparticle diffusion as mechanism for crystallization (for details see [66]).

Since the microscope was not equipped with an environmental cell, a reactor had to be used to anneal the Pt arrays in hydrogen and oxygen, with subsequent transfer to the microscope [66]. When an array of 40 nm Pt particles on SiO₂/Si(100) was heated in 1 bar H₂, no changes were detected up to 673 K but upon heating to 973 K for 3 h the Pt particles began to form larger crystalline domains (as in vacuum). The Pt array was also stable upon heating in oxygen to 973 K, but the onset of crystallization was already at about 700 K. Johansson et al. [67] suggested that the increased Pt mobility is presumably due to the surfactant action of oxygen, weakening the Pt-Pt bonds and allowing rapid Pt transport (probably as PtO_x). Heating in O₂ above 1000 K removes Pt by volatilization as PtO₂ (dry etching) and leads to a reduction in particle size [67]. In agreement with the study on epitaxially grown Pt particles, a high temperature hydrogen treatment lead to the formation of low index surface facets. However, since the EBL particles have rough surfaces already after preparation, surface roughening upon oxidation is difficult to detect (oxidation of already recrystallized particles was not performed).

All results presented show that supported metal nanoparticles can change their structure under reaction conditions. When the particle size is increased by sintering, the geometric (bulk and surface) as well as the electronic structure may change. Even when the size of the metal particles is unaffected, the presence of adsorbates (reactants) may alter the surface structure of individual particles, for instance, from a rough, stepped surface to smooth terraces and vice versa. Apart from the influence of adsorbates, thermal annealing is able to crystallize polycrystalline aggregates to form single crystals with smooth facets. Resulting from the decrease in the number of defects, grain boundaries, dislocations, etc the catalytic performance may change. Activating and rejuvenating treatments are intended to produce the desired surface site configuration by making use of these processes (apart from removing surface contaminants such as carbonaceous deposits).

4. High pressure CO adsorption on Pd/Al₂O₃ monitored by sum frequency generation spectroscopy

In the preceding chapter we have shown how the surface of metal nanoparticles restructures under reaction conditions, induced by gases and/or high temperature. It is obvious that this effect has a strong influence on the adsorption and turnover of reactants. However, even if the catalyst surface is unaffected and behaves rigid and simply "waits" for the reaction to occur, the structure of an adsorbate under reaction conditions is probably still different from UHV experiments. At the high pressure of a catalytic reaction surface coverages may be obtained that cannot be reproduced by the small exposures of surface science studies (typically on the order of langmuirs, 10^{-6} Torr s). If the "saturation" coverage of UHV experiments is exceeded, new adsorbate structures may form, as shown, e.g., by a high pressure STM study of CO on Pt(111) [24]. Furthermore, at high pressure weakly adsorbed species are present with much higher concentration (resulting from a higher rate of adsorption) than under low pressure when they quickly desorb [70]. In the most unfavorable case, prominent species of low pressure studies may simply be spectators under high pressure conditions.

In order to tackle this problem a surface sensitive technique is needed that allows to monitor adsorbates under reaction conditions (\sim 1 bar). A high pressure environment prevents the use of electron spectroscopies but is compatible with photon-based techniques such as infrared-visible sum frequency generation (SFG) spectroscopy. IR-vis SFG is a type of laser spectroscopy that is able to acquire vibrational spectra of adsorbates from UHV to ambient conditions. Due to its inherent surface sensitivity, surface vibrational spectra can be recorded even in the presence of a gas phase, in contrast to infrared reflection absorption spectroscopy (IRAS) that encounters problems with the excitation of rotational bands in the gas phase at pressures >1 mbar, obstructing the surface species information. A detailed description of the SFG process can be found in the literature [70–72]. SFG is a second-order nonlinear optical process which involves the mixing of tunable infrared (ω_{IR}) and visible light (ω_{vis}) to produce a sum frequency output ($\omega_{SFG} = \omega_{IR} + \omega_{vis}$). The process is only allowed in a medium without inversion symmetry (in the electric dipole approximation), e.g., at surfaces where the inversion symmetry is broken. The dominant SFG signal is hence generated by the modes of the adsorbate, while the centrosymmetric bulk of face-centered cubic metals and an isotropic gas phase give nearly zero contribution to the SFG signal.

It was already mentioned in the introduction that single crystals cannot fully represent supported metals. In order to include size and electronic effects, surface rearrangements, etc. in a pressure-dependent study of gas adsorption, SFG spectroscopy should be ideally carried



Figure 7. (a) SFG spectra of CO adsorption on a Pd/Al₂O₃/NiAl(110) model catalyst at 190 K (3 nm Pd particles grown at 90 K). The observed resonances are characteristic of bridge-bonded CO and terminally bonded CO; (b) shows the corresponding spectra acquired at 300 K. Terminally bonded CO can be re-populated at ≥1 mbar.

out on supported nanoparticles. Although the applicability of SFG spectroscopy to nanostructured supported catalysts has been questioned for several reasons (scattering of laser beams on rough surfaces, disordered adsorbates, small total coverages), we recently succeeded to obtain SFG spectra from CO adsorbed on supported Pd nanoclusters [73]. Pd/Al₂O₃/NiAl(110) model catalyst were prepared according to the procedure described in section 2.1 and transferred under vacuum to an SFG-compatible UHV-high pressure cell. Details about the sample preparation and cell design are published elsewhere [73,13].

Figure 7 shows SFG spectra of CO adsorption on alumina supported Pd particles of 3 nm mean size (about 300 atoms per particle), grown at 90 K (particle density 10^{13} /cm²). According to LEED and STM measurements [30,38], the particle surface exhibits a high defect density as a result of the low growth temperature. Figure 7(a) displays SFG spectra taken at 190 K. Two peaks are clearly identified at 10^{-7} mbar CO and, according to IRAS results on Pd single crystals [74–76], they originate from bridge-bonded CO at 1976 cm⁻¹ and from terminal (on-top) CO at 2106 cm⁻¹. If one takes the integrated SFG signal intensity as a measure of the ratio of on-top to bridged CO, a value of about 0.5 is obtained. However, this value is only taken as an estimate here, since

the SFG intensity cannot be easily correlated with the concentration of a particular surface species. The coexistence of bridge and on-top CO, a situation which is not found on Pd single crystals, reflects the defective structure of the Pd nanoparticles. In fact, the site occupancy on the Pd aggregates compares best with defect rich single crystal Pd(111) or rough Pd thin films [74,75,77]. The difference between supported Pd aggregates and Pd(111) could result from a reduced lateral CO interaction on the nanoparticles or from the presence of additional crystal planes.

Increasing the pressure to 1, 10 and 200 mbar CO had only a small effect on the peak frequencies and also the ratio of on-top vs. bridge CO was nearly unchanged (figure 7(a)). If the sample temperature is raised to 300 K (figure 7(b)), which is above the desorption temperature of ontop CO on Pd clusters under UHV conditions [30], bridgebonded CO is the only species that can be observed by SFG at 10^{-7} mbar. However, the on-top adsorption sites can be populated at $p \ge 1$ mbar, and at 200 mbar CO a relative ontop/bridge ratio of ~0.5 can be obtained, similar to the value at 190 K.

Comparing figures 7 (a) and (b) illustrates the pressureand temperature-dependent adsorption site occupancy of CO on Pd/Al₂O₃. While at 190 K an extrapolation of the 10^{-7} mbar spectrum to 200 mbar would lead to a satisfactory result, for a temperature of 300 K the prediction would be wrong (absence vs. presence of on-top CO). In addition, the adsorption site occupancy of Pd nanoparticles is influenced by the particle size and surface structure. If the same experiment is carried out on Pd particles grown at 300 K that mainly exhibit well-developed (111) surface facets, the adsorption behavior is again different [73]. These measurements could be repeated several times indicating that significant structural changes of the particles were absent – which seems reasonable at the low temperatures applied. Our adsorbates under reaction conditions. If this is carried out under several bars of pressure and at higher temperature even more pronounced effects are expected.

5. Conclusions

Noble metal nanoparticles cannot be simply considered as a rigid arrangement of metal atoms. Their lattice structure may be size-dependent and their surface may change upon gas exposure during the reaction or during activation/regeneration. High temperatures can restructure both the internal and surface structure of nanoparticles, an effect which is enhanced by the presence of adsorbates. At high pressure, adsorbate structures may be obtained that are not observed under UHV conditions. All effects listed so far have direct impact on the performance of a catalyst. The picture becomes even more complex when the different phenomena interact which each other or when metal–support interactions occur.

In situ studies under reaction conditions that monitor both the structure of the catalyst and of the adsorbates will be a major effort of future catalysis research. High pressure STMs, electron microscopes with environmental cells, and spectroscopic techniques that can work under high pressure are among the most promising tools able to interconnect fundamental surface science studies with applied catalysis.

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