Surface Science Approach to Catalyst Preparation Using Thin Oxide Films as Substrates

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Introduction

Molecular-level details about surface processes are difficult to obtain from industrially applied heterogeneous catalyst materials because of their structural and chemical complexity. Instead, one must resort to simplified models such as "dispersed model systems" (powders), or planar model systems that allow sophisticated surface characterization techniques to be applied. The "classical" surface science approach, which also represents the simplest model approach in terms of surface structure, uses metal single-crystal surfaces in combination with the power of available ultrahigh vacuum (UHV)-based microscopic and spectroscopic techniques to gain detailed atomic and molecular level understanding of catalytically relevant processes such as adsorption, diffusion and reaction, and their structure sensitivity.[1–3] This approach has, however, two main limitations, which are commonly referred to as pressure gap and materials gap: first, adsorption structures and reaction pathways observed under UHV conditions may not necessarily be the same as those present under realistic pressure conditions. And second, single-crystal metal samples do not cover important materials aspects of a technical catalyst such as particle size effects and the influence of the support. Therefore, several approaches have in recent years been put forward in order to overcome these limitations.[4–6]

New developments in experimental techniques enabled in situ studies under elevated pressure conditions. These include, for example, photon-based techniques such as polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) or sum frequency generation for vibrational spectroscopic characterization,[7] ambient pressure X-ray photoelectron spectroscopy (AP-XPS) for electronic structure characterization,[8] and high-pressure scanning tunneling microscopy (HP-STM) for morphological characterization.[9]

With the objective to include the influence of the oxide support as well as particle size effects, the surface science approach has been extended to model systems with increased materials complexity such as those represented by metal particles supported on flat oxide substrates.[10–14] A particular appealing approach in this respect is the utilization of thin, single-crystalline oxide films grown on metallic substrates as support for catalytically active metal nanoparticles. Because these support materials exhibit finite electrical conductivity even if the oxide in its bulk form has a large band gap, UHV-based analytical tools that rely on charged information carriers (electrons, ions) can be applied in a similar way as for metallic samples, allowing atomic-scale information of surface processes on these model catalysts to be obtained.[15] As an example, an MgO-supported Au thin-film model system and the individual stages of preparation viewed with scanning tunneling microscopy are presented in Fig. 1.

This particular example serves to demonstrate the enormous potential of the thin-film model approach for providing fundamental understanding of the surface properties. For Au/MgO(001), the combination of several experimental techniques, in particular STM, electron spin resonance, IRAS and temperature-programmed desorption (TPD), with computational studies using density functional theory, allowed the properties of the oxide surface, of metal atoms adsorbed on the oxide surface,[17] as well as of point defects on the oxide surface[18,19] and their interaction with metal atoms and particles[20] to be determined in greatest detail. In addition of being suitable model substrates for metal nanoparticles, the special properties of ultrathin oxide films and the catalytic activity intrinsic to these materials have come under scrutiny in recent years. Again for supported MgO thin films, Pacchioni et al. first demonstrated in a computational study that charge transfer from the metallic substrate through the ultrathin oxide film into an adsorbate on the oxide film is possible.[21] In addition to a sufficiently large electron affinity of the adsorbate, this process requires the work function of the metal to be lowered by the oxide film as well as the stabilization of the charged adsorbate by polaronic distortion in the oxide film. Experimental verification of this effect, which has its foundation in early work by Cabrera and Mott,[22] was provided soon after the theoretical prediction.[23,24] The observed high catalytic activity of a FeO film on Pt(111) in CO oxidation could also be explained based on this concept.[25]

The surface science approach to catalysis using oxide-supported metal nanoparticles and applying UHV as well as in situ characterization techniques has certainly contributed to deepen the understanding of processes in heterogeneous catalysis and provided also fundamental insight into the interaction of metal atoms and nanoparticles with the support material. The success of this approach is also based on the fact that UHV methodologies allow these model systems to be prepared and studied under ultraclean, contaminant-free conditions, which greatly simplifies the interpretation of results. In spite of the huge achievements in
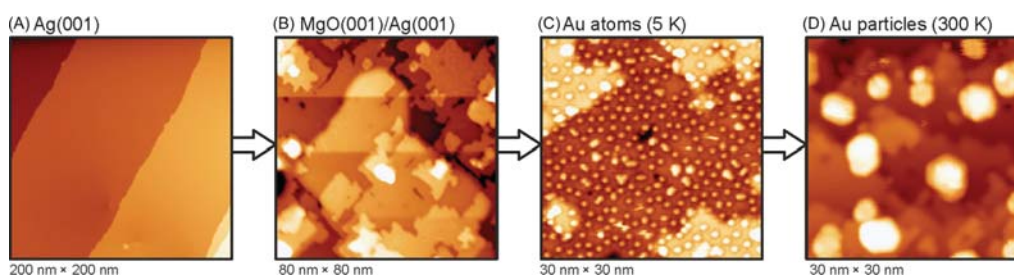
Fig. 1 Low-temperature (5 K) STM images of the various stages of Au/MgO(001)/Ag(001) model catalyst preparation. (A) Clean Ag(001) surface; (B) 8 ML MgO(001)/Ag(001) prepared by reactive deposition of Mg on Ag(001) in oxygen background. (C) Single Au atoms deposited at 5 K on a 8 ML MgO(001)/Ag(001) film. (D) Au particles on 8 ML MgO(001)/Ag(001) formed after annealing to 300 K. Taken from Sterrer, M.; Freund, H. J. Towards Realistic Surface Science Models of Heterogeneous Catalysts: Influence of Support Hydroxylation and Catalyst Preparation Method. *Catal. Lett*. **2013,** *143*, 375–385.

terms of materials complexity and realistic reaction conditions in the field of model catalysis, there still remain some open questions regarding the comparability to real-world catalyst materials. Among them is the influence of catalyst preparation method.

Model Studies of Supported Metal Catalyst Preparation

Almost all supported catalysts employed industrially are prepared by wet chemical methods.[26] The fundamental difference with respect to the UHV-surface science approach of catalyst preparation is the nature of the precursor and the way it is transformed into a nanoparticle. Fig. 2 highlights the various steps of the surface science and technical catalyst preparation procedures, respectively. In the case of a typical surface science experiment, the catalytically active metal is applied to the clean support by physical vapor deposition. The impinging metal atoms diffuse on the surface until a stable nuclei is formed either by trapping of atoms at defect sites or by dimerization. Agglomeration and sintering at elevated temperature then lead to the formation of nanoparticles (Fig. 2A). By contrast, the first step of catalyst preparation in a commonly applied wet chemical procedure consists of the interaction of the support with precursor solutions that contain the metal component in the form of salts or complexes. This is followed by drying, calcination, and reduction steps, which are necessary to transform the adsorbed metal precursor into the catalytically active phase (Fig. 2B).

Several different preparation procedures have been developed to obtain catalyst materials that meet the demands of specific catalytic processes. These include, among others, impregnation, coprecipitation, deposition–precipitation, and ion exchange. Many of those procedures consist of several complex steps with different phases being involved. For example, the application of the catalyst precursor to the support proceeds through different mechanisms in the procedures mentioned earlier. In impregnation,
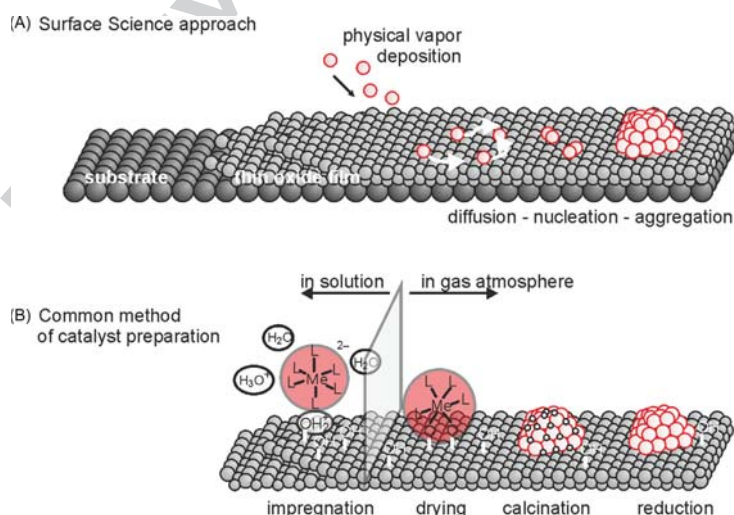

Fig. 2 Schematic representation of the individual stages of preparation of (A) a model catalyst in UHV, and (B) a technical catalyst.

which is commonly used to prepare supported noble metal catalysts, metal complexes are adsorbed from solution onto the support surface. The solution pH is adjusted to a value where metal complex and support surface exhibit opposite charge, allowing for electrostatic adsorption of the complex. Impregnation is usually performed in either of the following modes: dry/incipient-wetness impregnation, where the solution volume matches exactly with the pore volume of the support, or wet impregnation, which uses excess volume of solution.[27] In deposition–precipitation, which has originally been developed to obtain high loadings of metals such as Ni, Fe, or Co, selective precipitation of the precursor onto the support surface is achieved by transforming a highly soluble precursor into a compound with lower solubility through pH change.[28] During coprecipitation, the precursor and the support are simultaneously precipitated from solution by the action of a precipitating agent.[29] Subsequent to the initial adsorption of the precursor onto the support, several steps, which include washing, drying, calcination, and reduction, are required to transform the precursor into an active compound.[26] Studying the influence of preparation parameters on the catalytic activity is a common practice in catalysis research to find the best catalyst. By contrast, only a few groups in the world are engaged in studies related to the fundamental understanding of the connection between the physical and chemical properties of the working catalyst and the applied preparation conditions, which forms the basis for catalyst design.[30] Along the same line, surface science-related research into catalysis mainly focused on adsorption and reactivity on metal surfaces or on metal–support interactions, but studies related to catalyst preparation are rare.

While the processes during the formation of metal nanoparticles on oxide supports are reasonably well understood in the case of the surface science models,[10] the complexity of the materials and the lack of suitable analytical techniques render the detailed mechanistic elucidation of the individual steps in technical catalyst preparation a difficult task. Nevertheless, several models have been introduced that catch the essential aspects of the interaction of metal complexes with the support surface at the oxide–liquid interface.[30] To mention here are the "strong electrostatic adsorption" model by J. R. Regalbuto[31] (based on pioneering work by Brunelle[32]), which considers mainly an electrostatic adsorption mechanism of charged precursor complexes, and the "interfacial coordination chemistry" approach by M. Che,[33] which includes strong chemical bonding (grafting) of the precursor complexes to the support in addition to electrostatic adsorption. These models have proven valuable, for example, for explaining the dependence of metal loading as a function of preparation conditions.[34] The least understood process in technical catalyst preparation is the transformation of the precatalyst into the raw catalyst, that is, the decomposition of the adsorbed precursor during the calcination step. This was highlighted by Richard G. Finke in a recent review paper that discusses the existing literature in this area and where the following statement can be found: "Overall, surprisingly little is known about the mechanism(s) of formation of the desired size, shape, and compositionally controlled supported nanoparticle catalysts".[35] New developments in the field of in situ experimental techniques, such as magnetic resonance imaging,[36] X-ray differential pair distribution function method,[37] or environmental transmission electron microscopy,[38] promise to provide new insight into these processes.

Being aware of this shortage in understanding as well as of the importance of catalyst preparation in general, surface scientists have in the past undertaken several attempts to mimic catalyst preparation using flat substrates. For example, in an early work by Ertl et al. the preparation and characterization of vanadia species on a TiO_2 substrate that was obtained by oxidation of a thin Ti layer on a support was described.[39] Later on, several reports about carbon-based Pt catalysts investigated by STM appeared from the groups of Wolf[40,41] and Baiker,[42,43] Niemantsverdriet et al. reported on the preparation of supported catalysts on flat (amorphous) oxide substrates using a specifically designed spin coating technique,[44–46] which was later on used also by other.[47,48] Recently, Carrier et al. applied a surface science approach to prepare and characterize typical hydrotreating catalysts.[49–51] Reports on the characterization of the precursor interaction with single-crystalline oxide substrates should not be left out. These include an in-situ investigation of the adsorption of Pt–tetraammine complexes on a quartz(100) surface using surface X-ray reflectivity,[52] and a very recent report on the precipitation of Ni on α-Al_2O_3 investigated with grazing-incidence X-ray absorption.[53] Despite the wealth of information obtained with the above-mentioned surface science approaches, most of them have also several limitations: The use of insulating bulk single-crystal oxides imposes some restrictions as to the applicability of standard surface science methods, and with thin, amorphous oxide films (obtained, for example, by surface oxidation of a Si wafer) as substrates, a good part of the morphological control is lost. Thin, single-crystalline oxide films grown on metallic substrates, on the other hand, represent promising alternatives as substrates for model studies of catalyst preparation.

Surface Science Approach to Supported Catalyst Preparation Using Thin Oxide Films as Supports

In general, using a flat substrate as done in the surface science approach to catalyst preparation imposes a few restrictions with respect to the applicability of some wet chemical preparation routes. For example, pore volume or incipient wetness impregnation cannot be applied because of the absence of pores. In addition, some preparation routes such as deposition–precipitation require vigorous stirring of the support-precursor suspension. Because of the small volume of the precursor solution and the single crystal nature of the substrate, the conditions under which deposition precipitation is usually carried out cannot efficiently be achieved. Instead, a situation that is more analog to the wet impregnation technique, that is, exposing the surface to an excess amount of precursor solution, is applied in the model catalyst preparation described in this article.

A general outline of the approach to prepare model catalysts via wet-chemical methods and on the basis of single-crystalline oxide films as substrates is shown in Fig. 3. The approach is comprised of the following steps: (i) preparation of the thin oxide film used as support in UHV, (ii) transfer out of the UHV chamber and exposure to precursor solution, (iii) rinsing with a small amount of water, (iv) drying under a flow of He gas, (v) back-transfer into the UHV chamber and activation. The activation steps consist of
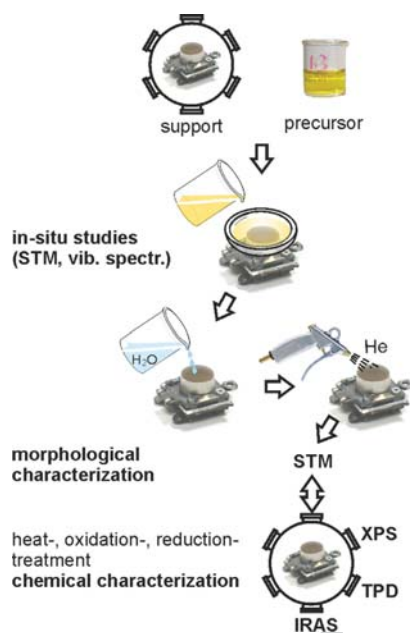
Fig. 3 Schematic representation of the surface science approach to catalyst preparation used in the present study.
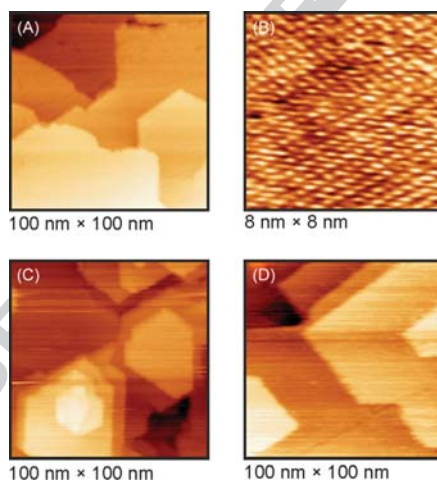

Fig. 4 (A) Large scale and (B) atomic resolution STM images of a $Fe_3O_4(111)$/Pt(111) film taken in air. (C) STM image of Fe_3O_4/Pt(111) after exposure to HCl(pH 2) solution. (D) STM image of $Fe_3O_4(111)$/Pt(111) after exposure to NaOH (pH 10) solution.[54,55]

stepwise decomposition of the adsorbed precursor by thermal treatments in UHV as well as oxidation and reduction treatments. The morphological and chemical properties of the precatalyst and the evolution of the final catalyst material during individual catalyst activation steps can then be probed, for example, by STM, XPS, TPD, and IRAS.

Our group has applied the wet-chemical catalyst procedure to various thin oxide film substrates, including $Fe_3O_4(111)$/ Pt(111),[54,55] MgO(100)/Ag(100),[56] and silica/Ru(0001).[57] In the following, results obtained for Pd on $Fe_3O_4(111)$/Pt(111) will be described in more detail.

The environmental stability of this surface was examined by STM. Fig. 4C shows an image of a freshly grown $Fe_3O_4(111)$ film after transfer from the UHV chamber into the EC-STM operated in air. The overall morphology of this surface is similar to corresponding results of UHV-STM studies[58] and, occasionally, atomic resolution of the top-most iron layer could be obtained even in ambient conditions (Fig. 4D).[55] Furthermore, this surface is also resistant against attack by acids or bases as demonstrated by the

STM images in Fig. 4E and F, which show that the surface morphology does not drastically change upon exposure to HCl (pH 2) or NaOH (pH 10), respectively.[54,55] This surface is, therefore, very well suited for studies of catalyst preparation.

With $Fe_3O_4(111)/Pt(111)$ as support, the preparation of supported Pd nanoparticles was studied. The choice of Pd is motivated by the importance of this metal in heterogeneous catalysis. The Pd salts most frequently applied as precursors in catalyst preparation are $PdCl_2$ and $Pd(NO_3)_2$.[59] $PdCl_2$ was used here because it can be applied in a wider range of pH values as compared to $Pd(NO_3)_2$, which is stable as molecular complex only in strongly acidic medium (pH 1) and forms colloidal particles already in the early stages of hydrolysis (>pH 1.5).[60]

The speciation of $PdCl_2$ in aqueous solutions has been the subject of intense research in the past. In strongly acidic conditions, the tetrachloro complex $PdCl_4^{2-}$ is the most abundant species. Upon hydrolysis, the chlorine ligands are gradually replaced by aqua or hydroxo ligands, leading finally to $Pd(OH)_4^{2-}$ species in strongly basic medium (Fig. 5, top).[61,62] Neutral Pd complexes of the kind $[PdCl_2(H_2O)_2]$ are formed at an intermediate stage of hydrolysis. These complexes are most probably responsible, because of their tendency for polymerization ($\rightarrow$polynuclear Pd–hydroxo complexes, PHC), for the formation of colloidal particles,[60] seen with the appearance of the dark brown color of the Pd solution at pH 4.7 in Fig. 5 (top). The pH at which formation of PHCs sets in can be slightly varied by changing the Pd^{2+} and Cl^- concentration. In alkaline medium and with very low Pd^{2+} (<0.5 µM) concentration the formation of PHCs can even be completely suppressed.

The strong influence of the solution pH on loading and morphology of deposited Pd is shown by means of the STM images displayed in Fig. 5 (bottom). These images were obtained after exposing $Fe_3O_4(111)$ films to precursor solution with the indicated pH for 60 min, and subsequent thermal treatment at 600 K in UHV, which transforms the adsorbed Pd precursor into Pd particles. First consider the samples prepared with the low pH solutions (pH 1.3–2.5), where the influence of PHCs can be excluded. The trend toward higher Pd loading and slightly increasing Pd particle size with increasing pH is obvious and in agreement with results obtained for similar preparations obtained with powder samples.[34,63] Within the "strong electrostatic adsorption" model which seems to be applicable for the given conditions (negatively charged precursor and positively charged support surface, $PZC(Fe_3O_4) \sim$ pH 6.5), the suppression of Pd precursor adsorption at low pH, which results in lower Pd loading, is typically explained by the lowering of the equilibrium adsorption constant as an effect of higher ionic strength of the strongly acidified precursor solution.[64] However, the solutions used here were of similar ionic strength, raising some doubts about this explanation. Alternatively, competitive adsorption of chloride on the strongly positively charged Fe_3O_4 surface at pH 1.3 could effectively screen the surface charge and, therefore, lead to less adsorbed Pd complexes.

While small and homogeneously distributed Pd particles result from exposure to the low pH solutions, high loading and large particles are obtained with the pH 4.7 precursor. At first glance, this result could be related to adsorption of colloidal particles present in the solution. However, deposited particles could not be identified by STM directly after deposition. The large amount of Pd adsorbed at this pH can most probably be related to a different interaction mechanism. Since at pH 4.7 the Fe_3O_4 surface is essentially uncharged and a considerable fraction of the solution species is charge-neutral, a strong chemical interaction via hydrolytic adsorption of precursor complexes could be the reason for the high Pd loading. With the basic pH 10 precursor solution
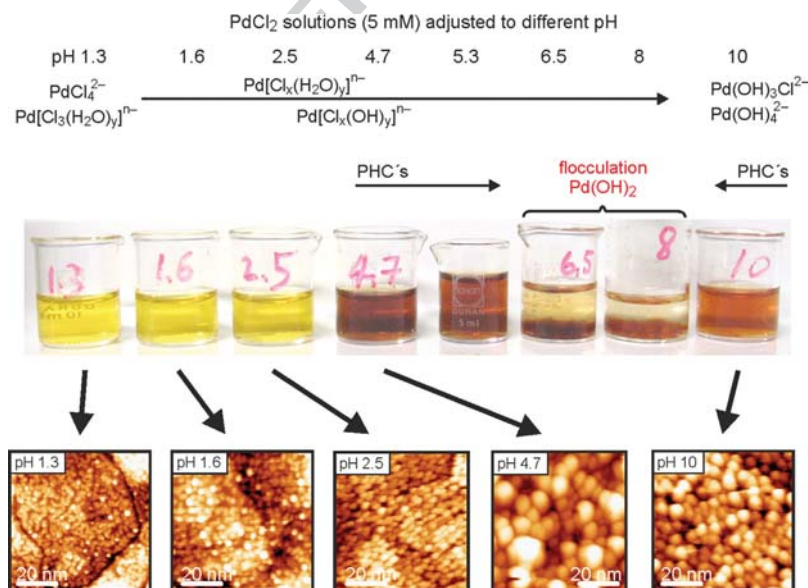

Fig. 5 (*Top*) Photograph of $PdCl_2$ precursor solutions adjusted to various pH. (*Bottom*) STM images (100 nm × 100 nm) of $Pd/Fe_3O_4(111)$ samples obtained after interaction of $Fe_3O_4(111)$ with the respective precursor solutions and subsequent annealing to 600 K (all images 100 nm × 100 nm).

the Pd loading decreased again and a more homogeneous particle size distribution is obtained compared to the pH 4.7 experiment. Since both the oxide surface and the solution complexes are negatively charged in this case, electrostatic adsorption is believed to play a negligible role and the adsorption of Pd occurs mainly via hydrolytic adsorption of the Pd–hydroxo complexes on the surface hydroxyl groups.

More detailed studies regarding the stepwise decomposition of adsorbed precursors and the formation of nanoparticles were conducted with samples prepared by exposure to pH 1.3 and pH 10 precursor solutions, respectively.[54,55] Those conditions were selected based on the following facts: Preparation of supported Pd catalysts by impregnation with acidic precursor solution is by far the most widely applied because it is the easiest and cheapest method for technical catalysts as well as for dispersed model systems (powders).[59] A serious limitation with the use of chlorine containing precursors is the contamination of the final catalyst with residual chlorine, which was reported to act as a catalyst poison in a number of catalytic reactions.[65–67] In order to avoid chlorine, recent studies focused on preparation of Pd catalysts by (modified) deposition–precipitation following in general Haruta's approach that yielded active Au catalysts.[68] In these studies, deposition of the precursor is brought about either by a classical deposition–precipitation approach with slowing adding a precipitating agent (e.g., Na_2CO_3 or NaOH) to an acidic support-precursor suspension, or by contacting the support directly with an alkaline precursor solution.[69–73] By applying pH 1.3 and pH 10 precursor solutions to the Fe_3O_4 surface and using microscopic (STM) and spectroscopic (XPS) characterization tools both the decomposition pathways of two different precursor species (Pd–chloro and Pd–hydroxo complexes, respectively) and the influence of chlorine and possible ways to remove it can, therefore, be elucidated (Fig. 6A and B).

A summary of the thermally induced precursor decomposition is presented in Fig. 7. In both cases, almost complete reduction of the precursor into metallic Pd nanoparticles was achieved by heating the samples up to 600 K in UHV. The decomposition pathway is, however, different for the respective precursor applied. It should be noted at this point that the adsorbed Pd–chloro and Pd–hydroxo complexes show up in XPS at a similar Pd 3d binding energy of 337.8 eV. Therefore, it is absolutely necessary to know the precursor speciation at the applied pH beforehand.

The Pd–chloro complexes were found to decompose directly into Pd nanoparticles. The Pd particles show no sign of sintering at the temperatures studied, are homogeneously distributed over the entire surface, and exhibit a narrow particle size distribution peaked at 2 nm.[54] Chlorine, which is bound to the precursor in the initial state, remains adsorbed on the surface even after complete decomposition into Pd nanoparticles. A blank experiment using a HCl solution without Pd precursor revealed that the Fe_3O_4 surface binds chlorine rather weakly under the conditions applied, which indicates that Cl remains mostly adsorbed on the surface of the nanoparticles and at the oxide–metal interface. In order to remove chlorine, the surface was subjected to an oxidation/reduction treatment at 500 K. Despite the low temperature applied (lower than the decomposition temperature), enhanced sintering was observed with an increase of particle diameter from 2 to 4–5 nm, a result that is explained on the basis of the formation of interface oxides that weaken the metal–substrate interaction.[74]

Alternatively, chlorine can be removed directly after the initial adsorption step by rinsing. This is demonstrated by the Pd 3d and Cl 2p XPS spectra in Fig. 8 obtained for a sample that was exposed to a pH 1.3 precursor solution (*black traces*) and that was subsequently rinsed with water (*red traces*). The disadvantage of this method of chlorine removal becomes directly evident by looking at the Pd 3d spectra: a considerable fraction of the precious metal is lost during the rinsing step.
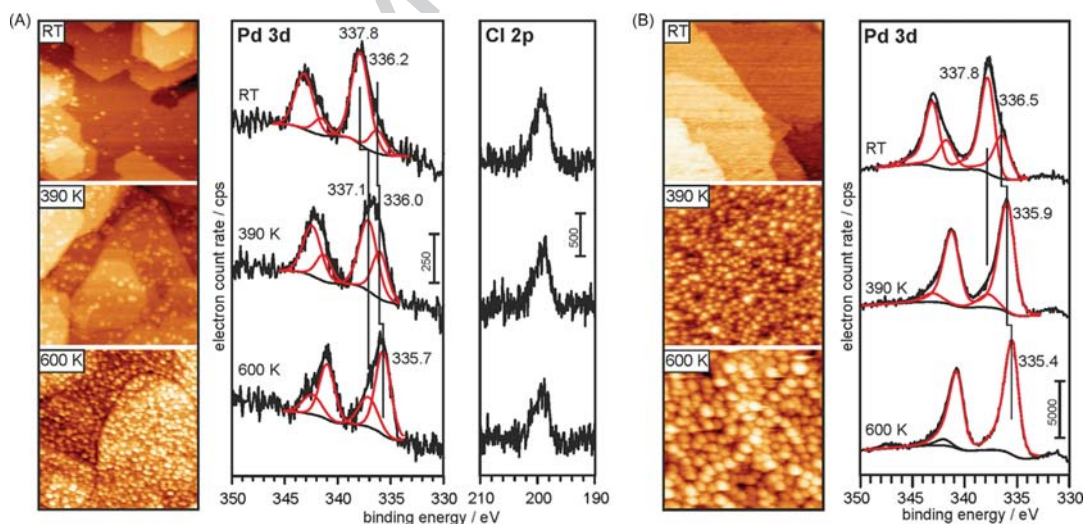

Fig. 6 STM images (100 nm × 100 nm) and XP spectra of $Fe_3O_4(111)/Pt(111)$ exposed to $PdCl_2$ precursor solution of (A) pH 1.3[54] and (B) pH 10[55] at room temperature and after subsequent annealing steps at 390 and 600 K.
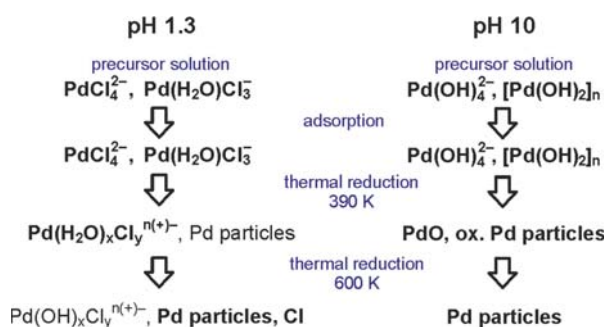
Fig. 7 Thermal decomposition pathways of Pd precursors present on $Fe_3O_4(111)$ after interaction with pH 1.3 (*left*) and pH 10 (*right*) precursor solution.
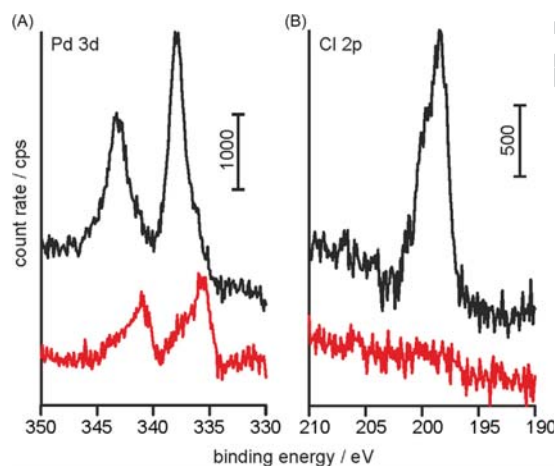

Fig. 8 Pd 3d (A) and Cl 2p (B) photoemission spectra of a $Pd/Fe_3O_4(111)$ sample prepared from acidic (pH 1.6) $PdCl_2$ precursor solution taken directly after removing the precursor solution (*black*) and after subsequent water rinsing (*red*).

In the case of Pd–hydroxo complexes adsorbed from a pH 10 precursor solution, the decomposition proceeds in two steps, via elimination of water from the hydroxo complexes to yield Pd-oxide particles at low temperature (390 K), and decomposition of the latter into Pd nanoparticles at high temperature (600 K).[55] As expected, this preparation leaves the final catalyst free of any residues (Na^+, Cl^-) from the applied precursor solution.

Once the possibility for wet-chemical preparation and subsequent characterization of supported metal catalysts on single-crystalline substrates has successfully been demonstrated, an important question that remains to be answered concerns the chemical properties of the catalyst and the comparison in terms of surface morphology to model catalysts that were prepared exclusively in UHV. As to the latter point, the size and shape distributions of the final Pd particles formed after heating to 600 K were analyzed for different Pd loadings that were obtained either by evaporation of different amounts of Pd on clean $Fe_3O_4(111)$ in UHV or by exposure of Fe_3O_4 to pH 10 precursor solutions for different times.[55] The corresponding STM images (Fig. 9A and C) show that the two preparation procedures yield qualitatively very similar results, except for a higher maximum particle density achieved in the solution preparation and different particle size distributions at the highest Pd coverage.

The support functionalization by hydroxyl groups in the solution experiment could be made out as the main source for these differences. The result of a simple experiment that provided the basis for this explanation is shown in Fig. 9. Here, STM images of Pd/Fe_3O_4 samples prepared by applying three different methods are compared: (a) a sample prepared exclusively in UHV, (b) a sample prepared by exposure of Fe_3O_4 to a blank pH 12(NaOH) solution and subsequent deposition of Pd in UHV, and (c) a sample prepared by exposure to pH 10 precursor solution. Because of the similar surface morphology of samples (b) and (c) it was concluded that for the given preparation conditions only the chemical properties of the support matter, and the nature of the precursor is of secondary importance in determining the final state of the samples.[55]

The final step of catalyst preparation consists of chemical characterization and the elucidation of catalytic activity of the activated catalyst material. XPS and CO chemisorption as analyzed with IRAS and TPD were used to characterize Pd/Fe_3O_4
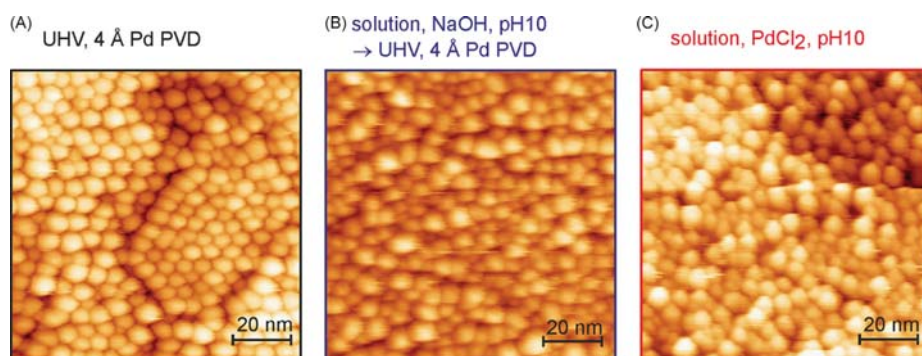
Fig. 9   STM images (100 nm × 100 nm) of Pd/Fe$_3$O$_4$(111)/Pt(111) samples obtained by different preparation procedures: (A) Deposition of Pd by physical vapor deposition on a freshly prepared Fe$_3$O$_4$(111) film in UHV. (B) Deposition of Pd by physical vapor deposition on Fe$_3$O$_4$(111) that has previously been exposed to NaOH(pH 12) solution. (C) Deposition of Pd on Fe$_3$O$_4$(111) by interaction with PdCl$_2$(pH 10) precursor solution. All STM images were obtained after annealing to 600 K. Adapted from Wang, H. F.; Kaden, W. E.; Dowler, R.; Sterrer, M.; Freund, H. J. Model Oxide-Supported Metal Catalysts—Comparison of Ultrahigh Vacuum and Solution Based Preparation of Pd Nanoparticles on a Single-Crystalline Oxide Substrate. *Phys. Chem. Chem. Phys.* **2012,** *14*, 11525–11533.

model catalysts prepared from pH 10 precursor solutions and activated by reduction in, respectively, CO or H$_2$ atmosphere. Reduction in CO led to CO chemisorption characteristics that are typical for supported Pd nanoparticles and are comparable to previous results obtained for Pd/Fe$_3$O$_4$ model systems prepared in UHV.[75] The CO chemisorptive properties of the catalyst changed, however, significantly upon H$_2$ reduction. Analysis of IRAS and XPS data after H$_2$ reduction indicated the formation of bimetallic Pd—Fe nanoparticles as a result of a strong metal–support interaction (SMSI). This modification can be easily understood on the basis of the catalytic action of Pd in providing H atoms for reduction of the Fe$_3$O$_4$ support via H$_2$ dissociation and H spill-over. Iron atoms from the reduced support then migrate into the Pd particles.[55]

The catalytic activity of the model catalysts in CO oxidation was investigated with temperature-programmed reaction.[16] Particular attention was paid to the differences between the regular catalyst and the one in the SMSI state. Since Fe$_3$O$_4$ is a reducible oxide with oxygen storage potential, the involvement of lattice oxygen in CO oxidation (→ Mars-van Krevelen type mechanism) was first explored by looking at the CO$_2$ production in a CO-TPD run. Indeed, and in agreement with earlier studies,[76] the sample activated by oxidation and CO reduction gave rise to a CO$_2$ signal at around 500 K (Fig. 10). By contrast, no CO$_2$ could be detected from the SMSI sample. The weak bonding of CO to the bimetallic particles can be ruled out as explanation for the lack of reactivity on the basis of the results for the CO oxidation reaction described later. It is rather the unavailability of lattice oxygen in the reduced near-surface regions that is responsible for the lack of activity in this type of reaction.
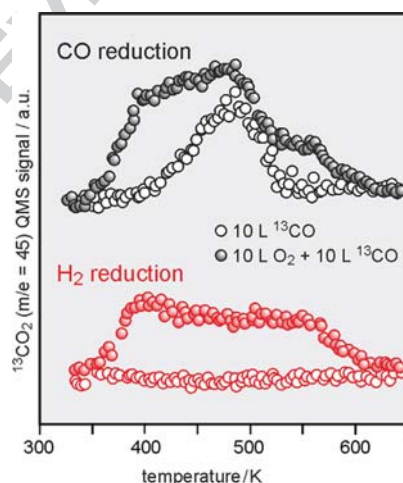
Fig. 10 ^{13}CO$_2$ TPD spectra obtained from model catalysts activated by CO reduction (*top*) and H$_2$ reduction (*bottom*) after dosing ^{13}CO (open circles) or ^{13}CO + O$_2$ (*filled circles*) at room temperature. Taken from Sterrer, M.; Freund, H. J. Towards Realistic Surface Science Models of Heterogeneous Catalysts: Influence of Support Hydroxylation and Catalyst Preparation Method. *Catal. Lett.* **2013,** *143*, 375–385.

If molecular oxygen is predosed, enhanced CO_2 production is observed on both samples (Fig. 10, *filled circles*). It is noted that the CO_2 signal arising from the sample activated by oxidation and CO reduction appears to be the sum of two contributions: one from a reaction of CO with lattice oxygen with a maximum at around 500 K, and the other one from the reaction of CO with dissociated oxygen on the Pd particles, which exhibits a maximum at 400 K and extends to 550 K. Since the former contribution is missing on the sample prepared by reduction in H_2 atmosphere, only the catalytic CO oxidation path is observed in this case. Similar CO_2 yields were obtained for both samples under the experimental conditions applied here (O_2 and CO were dosed at room temperature), which indicates that the catalytic activity of the sample in the SMSI state (H_2 reduction) is not particularly different from that of the regular one.

Concluding Remarks

Surface science investigations have strongly contributed to the understanding of catalytically relevant processes. The strength of the surface science approach is rooted in the possibility to have ultimate control over the morphology of the model surfaces (metal single crystals), allowing structure–reactivity relationships to be established. New challenges in the characterization and interpretation of surface functionality arise as we move on to more complex surfaces and interfaces. In this article, we highlighted recent surface science work in the field of oxide-supported metal nanoparticle model catalysts that put emphasis on catalyst preparation using wet-chemical procedures. The results presented demonstrate the feasibility of surface science investigations related to catalyst preparation utilizing single-crystalline, thin oxide films as supports. Various steps of the catalyst preparation procedure, from the clean support surface, via decomposition of the precursor, and finally to characterization and catalytic activity of the activated model catalyst, could be analyzed with typical surface science techniques. In the future, this approach shall be extended to in situ studies of the solid–liquid interface, which aim at exploring the initial state of catalyst preparation, namely, the interaction of precursor complexes with the support surface at the oxide–solution interface, at the molecular level.

Acknowledgment

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