ELSEVIER

Surface Science 500 (2002) 271–299

SURFACE SCIENCE

www.elsevier.com/locate/susc

Clusters and islands on oxides: from catalysis via electronics and magnetism to optics

Hans-Joachim Freund *

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Received 5 July 2000; accepted for publication 27 April 2001

Abstract

The study of metal deposits on oxides represents a field of wide interest with respect to applications as well as to basic science. The state of the art of the field is reviewed on the basis of examples from various research groups. An attempt is made to define and discuss a series of new experiments that could be undertaken to answer some key questions in the field. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Models of surface chemical reactions; Catalysis; Surface diffusion; Aluminum oxide; Clusters; Insulating films

1. Introduction

Why in the world would anyone be interested in a rather specific subject like this? There are many reasons why you should be interested and those range from the industrial importance of catalysis to the beauty of the pre-Roman art of making stained glasses:

(1) Think about your car and the pollution control in the exhaust system. Fig. 1 shows a schematic diagram with a typical exhaust catalyst in its housing [1]. The catalyst consists of a monolithic backbone covered internally with a washcoat made of mainly alumina but also ceria and zirconia, which itself is mesoporous and holds the small metal particles, often platinum or rhodium. An electron microscope allows us to take a close look at the morphology of the catalyst at the nanometer scale. In order to be active, the metal particles have to be of a few nanometer in diameter and also the support has to be treated in the right way. To a certain extent the preparation is an art, some call it even “black magic”. A full understanding of the microscopic processes occurring at the surface of the particles or at the interface between particle and support, however, is unfortunately lacking. We have to realize that catalysis in connection with pollution control—the specific example chosen here—does only utilize a small fraction of the world market for solid catalysts. Human welfare is considerably depending on automotive, petroleum and other industries which constitute a market of $100 billion per year and growing rapidly. Given the situation, it is clear that we eventually must achieve a good understanding of the processes. Interestingly, even though the problem is strongly connected to applications, there is a lot of fundamental insight that has to be gained.

---

* Tel.: +49-30-84134102; fax: +49-30-84134101.
E-mail address: freund@fhi-berlin.mpg.de (H.-J. Freund).

0039-6028/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0039-6028(01)01543-6

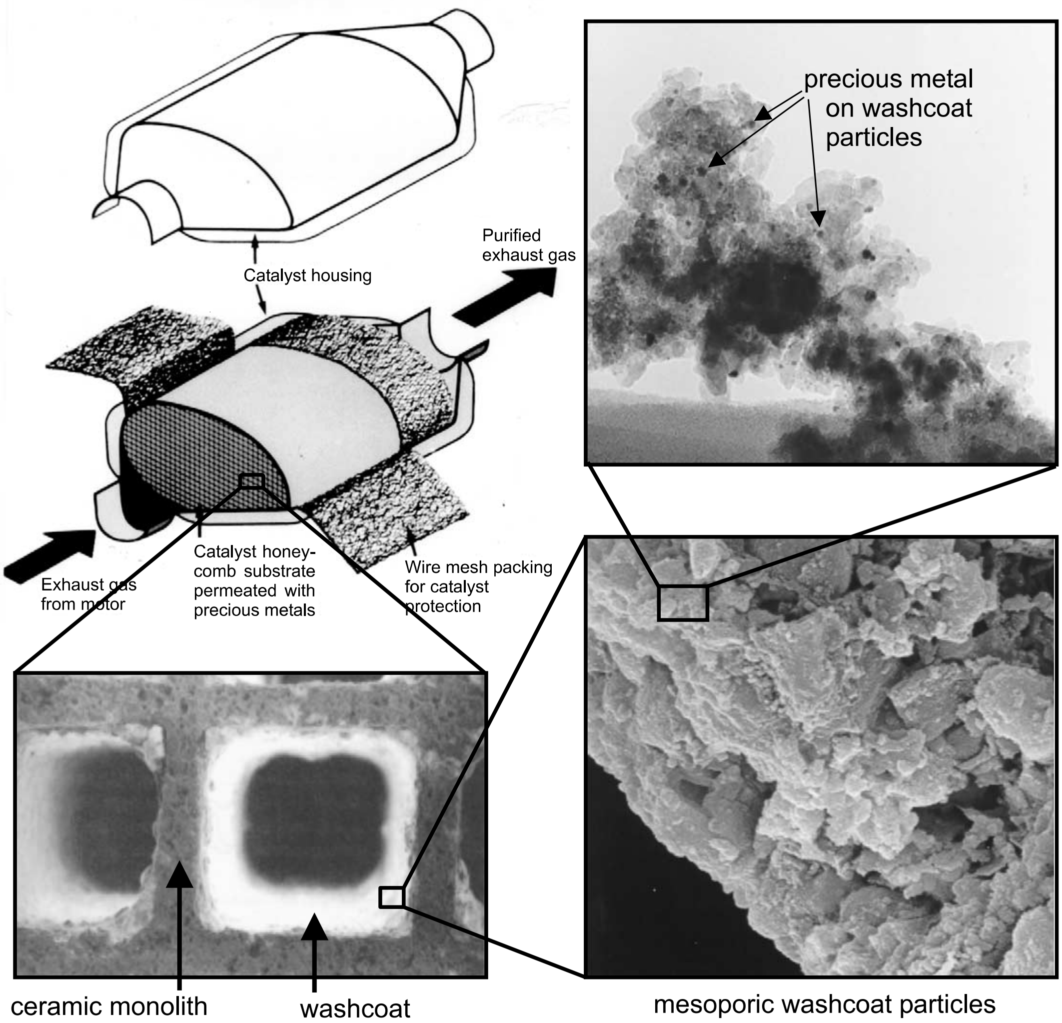

Fig. 1. Schematic representation of the car exhaust catalyst in its housing. Transmission electron micrographs with increasing resolution show the various constituing ceramic and metallic materials in their morphology. Adapted from Ref. [1].

(2) Think about the problem how one could create an artificial nose! Sensors [2–4] allow a computer to smell via "communication with a chemical reaction". An example is shown in Fig. 2. A schematic representation of a device which is called a metal-oxide-semiconductor-field-effect-transistor (MOSFET) is shown (Fig. 2a). In such a device a thin metal film is separated from a Si-crystal through an isolating layer of SiO_2. The idea is to modulate the conductance of a small semiconductor slice by means of an electric field perpendicular to the semiconductor surface. A positive charge on the metal layer induces a negative charge in the semiconductor resulting in a change in the lateral conduction. The charging of the metal layer critically depends on its morphology and can be influenced in a characteristic way by adsorbing gases onto it. These changes upon adsorption allow the MOSFET to "smell", but the details of the elementary steps are not fully understood. The actual device, which was developed about half a century after the initial idea, looks more like the one

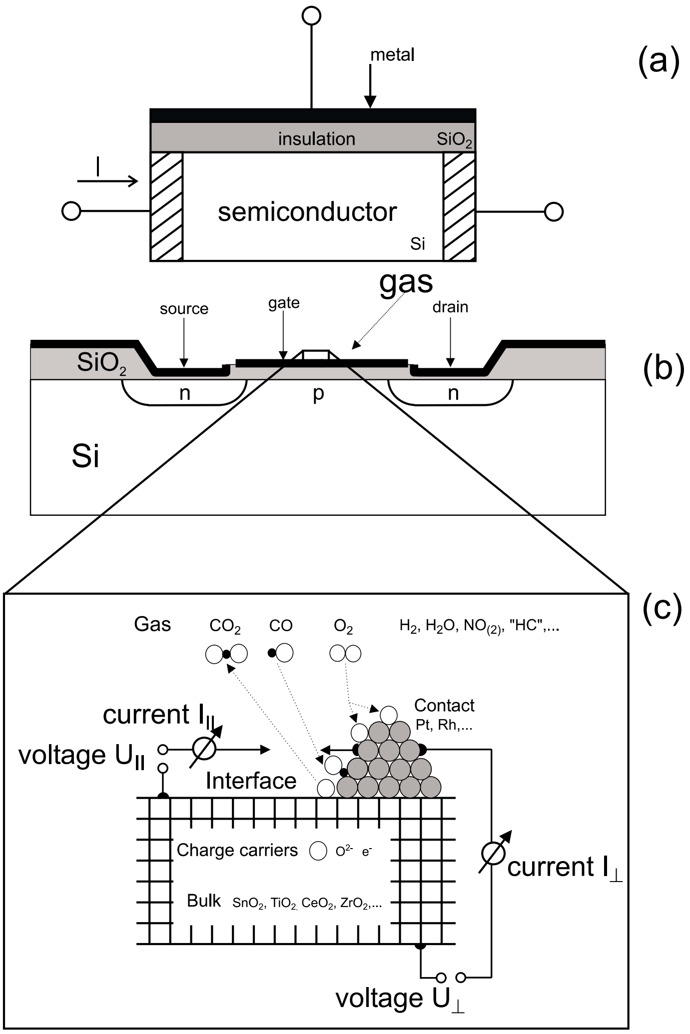

Fig. 2. (a) Schematic representation of the principle of a metal oxide field effect transistor (MOSFET). (b, c) Schematic representation of the design of a MOSFET, and representation of the morphology and the adsorption processes at the metal–oxide interface (2c adapted from Ref. [2]).

schematically shown in Fig. 2b. A n/p/n-transistor is generated via local doping of the semiconductor. It is possible to shape the oxide film and the metal layer as indicated, thus forming a source-gate-drain-structure. It is now easy to envision that the performance, durability and chemical sensitivity of such a device depends heavily on the microscopic structure of the metal layer (see Fig. 2c). The control of the structure of the metal overlayer film inturn depends on our understanding of the elementary steps in nucleation and growth of metal islands and their coalescence to form the film. Cluster formation is an intermediate step in this process, in fact a rather important one. In the series of elementary steps governing the shape size and distribution of islands cluster formation is crucial. The changes in conductance, i.e. the ability and sensitivity to “smell”, via the interaction with a gas phase, depends largely on the shape and size of islands, exposure of facets, and other more complex factors, such as co-adsorbates, contaminants etc. of the film. These properties need to be investigated.

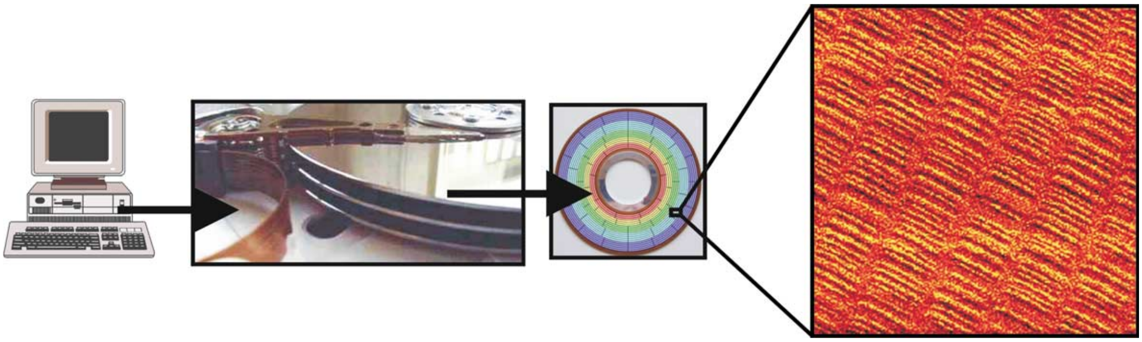

Fig. 3. Picture of a hard disk in a personal computer. At the right the sectors of a hard disc are schematically represented and in addition a small area consisting of magnetic nanoparticles is imaged on the far right.

(3) Think of the way magnetic materials are used to store information [5]! In Fig. 3 the situation is illustrated for a hard disc in your personal computer, be it used for science, business or entertainment. On the right the magnetic particles in one sector of the hard disc have been imaged. These particles are 650 nm long and 50 nm wide for a storage density of about 20 Gbit per inch^2. Their size can go down to 150×15 nm^2. A current goal is to make them even smaller. Magnetic recording industries make use of the fact that the ferromagnetic state of a material with a given orientation of the magnetic moment has a permanent magnetization if the material exists as nanometer-sized particles. Although this knowledge has been around since 40–50 years, despite intense activities, the difficulty in making small enough particles of good quality has slowed down the advancement of this applied field. Only recently, this difficulty in making small particles has been overcome and new experimental techniques have been developed. Conceptually, the ferromagnetic state of bulk metals is a surprisingly rarely observed property if we consider that most atoms have non-zero magnetic moments or spin. Apparently, the formation of metallic bonds leads to non-magnetic bulk metal. It appears quite natural to ask how the spin systems of clusters evolve as a function of particle size. Do we understand this in detail? The answer is probably No! Therefore we need deeper insight into the magnetic behavior of nanoparticles, which is potentially important for the development of new fundamental theories of magnetism and in modeling new magnetic materials for permanent magnets or high density recording as to above. Questions such as i) How small can we make a ferromagnet? ii) Can clusters of non-ferromagnetic materials be ferromagnetic? If yes, how many atoms do we need? iii) In which way does the interaction of a cluster with a substrate alter the magnetic properties? Can now be explored.

(4) Think of the Romans! Do you know how they made the beautiful stained glasses or how the glass for colossal, colorful windows in medieval cathedrals have been manufactured? It is based on cluster technology, i.e., the use of clusters interacting with oxidic substrates! Fig. 4 shows details of a window from the Altenberg Cathedral near Cologne. The red color is caused by gold particles embedded in the glass matrix and the matrix is an amorphous silica–alumina mixture. Since the work of the physicist A. Mie, published in "Annalen der Physik" in 1908 [6], it is understood that absorption of light in a collective excitation of electrons on a sphere of metal—we now call it a plasmon excitation—is the cause of the color. When the particles become smaller and smaller in size the electrons start to "realize" that they are confined in space and then the optical properties become size dependent in a way that has not been predicted by classical Mie-theory but is a consequence of quantum mechanics: If you put an electron in a "box", i.e. a potential well and the dimensions of the "box" reach atomic dimensions, e.g. 10 Å or so, then the states

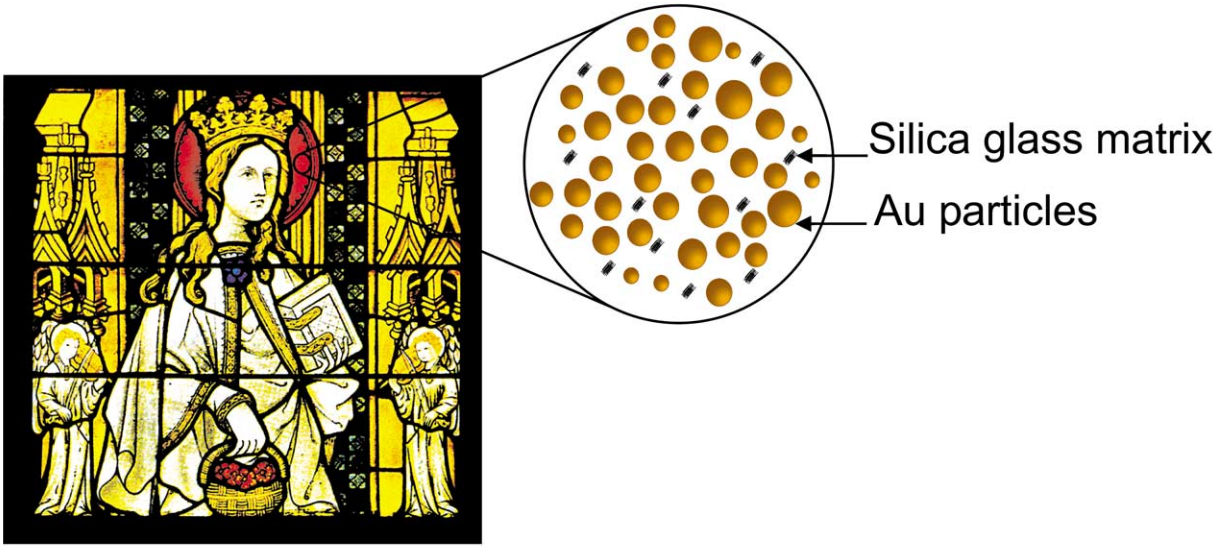

Fig. 4. Detail of a window in the Altenberg Cathedral (near Cologne). The red colored stained glass consists of small gold colloid particles residing in a glass matrix.

of these electrons in the box are not continuous but quantized. The energetic separation between the quantized levels are now depending on the size and therefore the energies for electron excitation will depend upon size, and, as it turns out, also on shape. This opens possibilities for manipulation of optical properties. If one, for example, asymmetrically stretches a solidifying glass the particles assume a certain shape which not only influences the optical absorption energy but also its polarization. Optical polarization filters [7] can be produced. While these filters depend on the linear optical properties of the material, also the non-linear optical responses are changed if high light intensities, e.g. from laser sources, are used. Keep in mind that the "matrix" surrounding the particle, in our case the glass, has an influence on the optical properties of the small particles so that there are many parameters that can be manipulated in order to design new materials with unexpected optical properties.

The chosen examples all have a connection to everyday life, including information transfer and storage, environmental pollution control, arts and even entertainment. It should be obvious therefore that though the topic is specific it has wide implications, and:

You must be interested!

In the following we discuss a variety of case studies and then in the final chapter speculate about things to do and where the field is going.

2. Where do we stand?

This question is answered in two steps. The first concerns the insulating substrate. How well do we understand its structure and properties? This is of importance to understand any modification to the substrate by deposition of additional material. In the second step, we deal with similar questions for the metal deposits, sometimes also called aggregates or clusters.

2.1. The oxide support

Let us start with a look at the oxide supports and answer the question: How do you make oxide surfaces? The preparation of a clean oxide surface is a rather difficult task. Several strategies have been followed [8–10].

The most straightforward strategy is in situ cleavage under ultrahigh-vacuum conditions. This, however, only leads to good results in certain

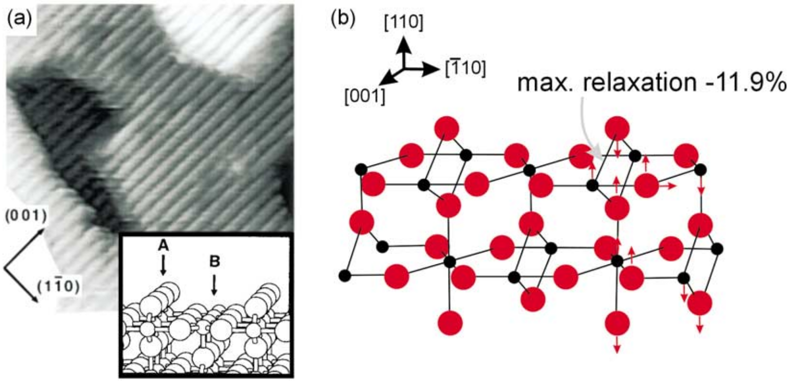

Fig. 5. Structure of $TiO_2(1\,1\,0)$ (1×1) surface as determined via STM (a, reproduced from Ref. [16]) and via grazing incidence X-ray scattering (b, adapted from Ref. [23]).

cases, such as MgO, NiO, ZnO, $SrTiO_3$, [11]. Some interesting materials such as Al_2O_3, SiO_2, TiO_2, etc. are hard to cleave, i.e., they tend to form rough surfaces upon cleave [10]. A general disadvantage of cleaved bulk single crystal insulators with respect to experimental investigations is their low thermal and electrical conductivity. An alternative way of bulk single crystal surface preparation is ex situ cutting and polishing followed by an in situ treatment by sputtering and subsequent annealing in oxygen. Through such a process a sufficient number of defects is created in the near surface region and in the bulk to support conductivity of the material. This leads to a situation where electron spectroscopies as well as scanning tunneling microscopy (STM) can be applied to elucidate the electronic and geometric structure of the system [10].

Single crystalline oxide surfaces also may be prepared via the growth of thin oxide films on single crystal metal supports [8,9,12]. To such systems all surface science tools can be applied directly. If the oxide film is supposed to represent the bulk situation special care has to be taken in the control of film thickness because the film should represent the situation in the bulk. Also, if adsorption and reactivity studies are intended the continuity of the film has to be guaranteed. There are several examples in the literature where this has been achieved [12–14]. Probably, the best-studied clean oxide surfaces are $TiO_2(1\,0\,0)$ and $TiO_2(1\,1\,0)$ [8,10,15]. A STM image of the clean (1×1) $TiO_2(1\,1\,0)$ surface taken by Diebold et al. [16] is shown in Fig. 5. One of the first atomically resolved images of this surface was reported by Thornton and co-workers [17,18]. The inset shows a ball and stick model of the surface. There is now accumulating evidence from theoretical modeling of the tunneling conditions, but also from adsorbate studies using molecules which are assumed to bind to the exposed Ti sites, that the bright rows represent Ti atoms. Iwasawa and co-workers [19–22] have successfully used formic acid in such a study and showed in line with the theoretical predictions, and counter intuitive with respect to topological arguments, that the Ti-ions are imaged as bright lines and the oxygen rows as dark lines. Taking the resolvable interatomic distances within the surface layer the values correspond to the structure of the stoichiometric (1 1 0) surface [23,24]. Interatomic distances normal to the surface, however, are substantially different from the bulk values as revealed by X-ray scattering experiments [23]. The top layer sixfold coordinated Ti atoms move outward and the fivefold-coordinated Ti atoms inward. This leads to a rumpling of 0.3 ± 0.1 Å. The rumpling repeats itself in the second layer down with an amplitude of about half of that in the top layer. Bond length variations range from 11.9% contraction to 9.3% expansion. These strong relaxations are not atypical for oxide surfaces and had been theoretically predicted [25–27].

Recently, the $RuO_2(1\,1\,0)$ surface, which is isostructural with the $TiO_2(1\,1\,0)$ surface, has been characterized via STM and low energy electron diffraction (LEED) as a means to determine structures [28,29]. It appears that in this case the contrast in the STM images has been reversed as compared with the $TiO_2(110)$ surface. The oxygen rows on the $RuO_2(110)$ surface are protruding while the ruthenium rows appear dark. In this case, CO adsorption has been used to show this, i.e. CO resides in the dark Ru rows. The structural relaxations as documented in the LEED studies are similar to the $TiO_2(110)$ surface.

There are several experimental results [30–33] where relaxations are particularly pronounced [25–27] basically corroborating the theoretical predictions although the quantitative agreement is not always good [34–37]. Specifically, the (0001) surfaces of materials such as Al_2O_3 [34,35], Cr_2O_3 [36] and Fe_2O_3 [37] have been studied with X-ray diffraction, quantitative LEED as well as with STM and theoretical methods. Fig. 6 shows the results of structural determinations for the three related systems $Al_2O_3(0001)$, $Cr_2O_3(0001)$ and $Fe_2O_3(0001)$ as addressed above. In all cases a stable structure in UHV is the metal ion terminated surface retaining only half of the number of metal ions in the surface as compared to a full buckled layer of metal ions within the bulk. The interlayer distances are strongly relaxed down to several layers below the surface. The perturbation of the structure due to the presence of the surface in oxides is considerably more pronounced than in metals, where the interlayer relaxations are typically of the order of a few percent [38]. The absence of the screening charge in a dielectric material such as an oxide contributes to this effect considerably. It has recently been pointed out [39] that oxide structures may not be as rigid as one might think based on the relatively high energy needed to excite lattice vibrations in the bulk.

Bulk oxide stoichiometries depend strongly on oxygen pressure, a fact that has been recognized for a long time [40]. So do oxide surface structures and stoichiometries [37]. In fact, if a Fe_2O_3 single crystalline film is grown in low oxygen pressure, the surface is metal terminated while growth under higher oxygen pressures leads to a complete oxygen termination [37]. Calculations by the Scheffler group [37] have shown, that a strong rearrangement of the electron distribution as well as relaxation between the layers leads to stabilization of the system. STM images by Weiss and co-workers [37] corroborate the coexistence of oxygen and iron terminated layers and thus indicate that stabilization must occur.

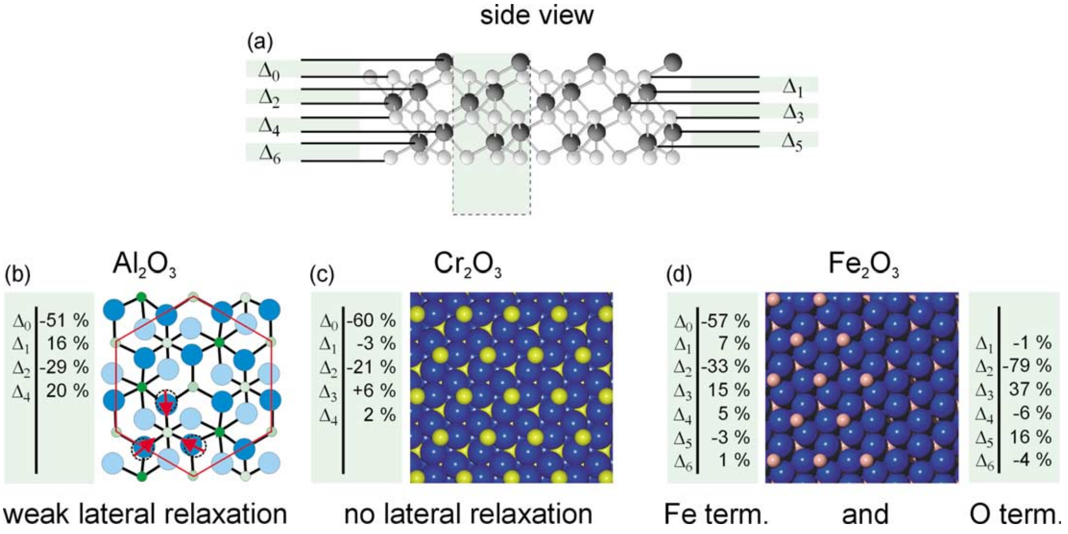

Fig. 6. (a) Experimental data on the structure of corundum-type depolarized (0001) surfaces (side and top views). (b) Adapted from Ref. [24], (c) Refs. [31,32], and (d) Ref. [37].

Another important stabilization mechanism for oxygen terminated surfaces proceeds via chemical means. Charge reduction can occur by replacing oxygen at the surface by hydroxyls. On the basis of energetic considerations [41], real crystallites must be terminated partly by polar surfaces, the charges of which are reduced by surface OH groups. The experimental confirmation was delivered much later [42,43]. For Al_2O_3 surfaces with oxygen termination it was shown recently by theoretical methods that OH termination also leads to the most stable surfaces [44]. Since hydrogen is difficult to detect with structural methods [24], vibrational spectroscopies are well suited to study this aspect. In fact, hydroxyl groups may be used to modify the chemical nature of oxide surface which in turn, has consequences for the adsorption of further material such as metal deposits [45,46]. We show in Fig. 7 the results of such a hydroxylation as measured with vibrational spectroscopies. Vibrational spectra can be measured either by infrared absorption after reflection of infrared light from the surface and recording the spectra with an interferometer (Fourier-transform infrared spectroscopy, FTIR) or by scattering electrons from the surface and measuring the loss of energy due to excitation of vibrations (electron energy loss spectroscopy, HREELS) [45,46]. In the case of a thin alumina film on NiAl(1 1 0) it was impossible to hydroxylate the oxide just by water dissociation, while on a similar film on NiAl(1 0 0) [47] formation of OH from dissociative H_2O adsorption occurs. The clean oxide film surface was exposed to metallic aluminum and then the aluminum was hydrolyzed via water adsorption to form a hydroxyl overlayer [45,46]. In Fig. 7 at the bottom a HREEL-spectrum showing the hydroxyl vibration at 465 meV (3750 cm^{-1}) is plotted atop a corresponding spectrum of the clean film. The peaks below 120 meV are due to the alumina vibrations [48]. The observed hydroxyl vibration energy coincides nicely with the FTIR absorption observed for the same system. In this case more water was adsorbed so that a broad band from water clusters is seen also. The sharp band at 3705 cm^{-1} is due to free OH groups at the surface of these water clusters [49], as they are known from the surface of ice. In fact, if a thick ice film is grown on the alumina film this particular vibration is observed (see Fig. 7). In comparison with literature data [50] it is now possible to assign the hydroxyl loss on the alumina surface. According to a review article by Knözinger and Ratnasamy [50] an OH-vibration at 3750 cm^{-1} is characteristic of hydroxyls bridging aluminum ions both in octahedral, or one in an octahedral and one in a tetrahedral site. On alumina films grown on a different NiAl substrate other types of OH species may be formed [47].

2.2. The metal particle–oxide system

So far, we have been considering the clean oxide surface and its reactivity. In the following, we consider the modification of the oxide surface by deposition of metals.

Over the last years several strategies have been followed [51]. Small metal particles have been deposited onto oxide bulk single crystal surfaces, particularly MgO, and characterized by transmission electron microscopy (TEM). A transmission electron micrograph is produced by transmitting electrons with an energy of several hundred (typically 200–400 keV) kiloelectronvolts through a sample using the contrast produced by the electron density in the system for imaging. Helmut Poppa has been the pioneer in the field of imaging small metal particles [52]. Contributions to it have been recently reviewed by Claude Henry, who himself was involved in the early TEM measurements [53]. A beautiful example from his group is reproduced in Fig. 8, showing the crystal shapes of the deposits with the largest ones being 150×150 nm^2 in size [54]. While these efforts were mainly aimed at preparing small well defined particles, another strategy is preparing thin metal films on bulk oxide single crystals, such as TiO_2(1 1 0) surfaces [55–58]. Several groups [59–61] have started to investigate metal deposition on TiO_2 surfaces. Interesting initial results concerning metal particle migration, and oxide migration onto the metal particles have been obtained [60,61]. Particularly well suited for the application of STM are metal particles deposited onto thin film oxide surfaces [12,13, 53,62].

Often, well-ordered alumina films have been used as substrates. In Fig. 9 we show the result of a

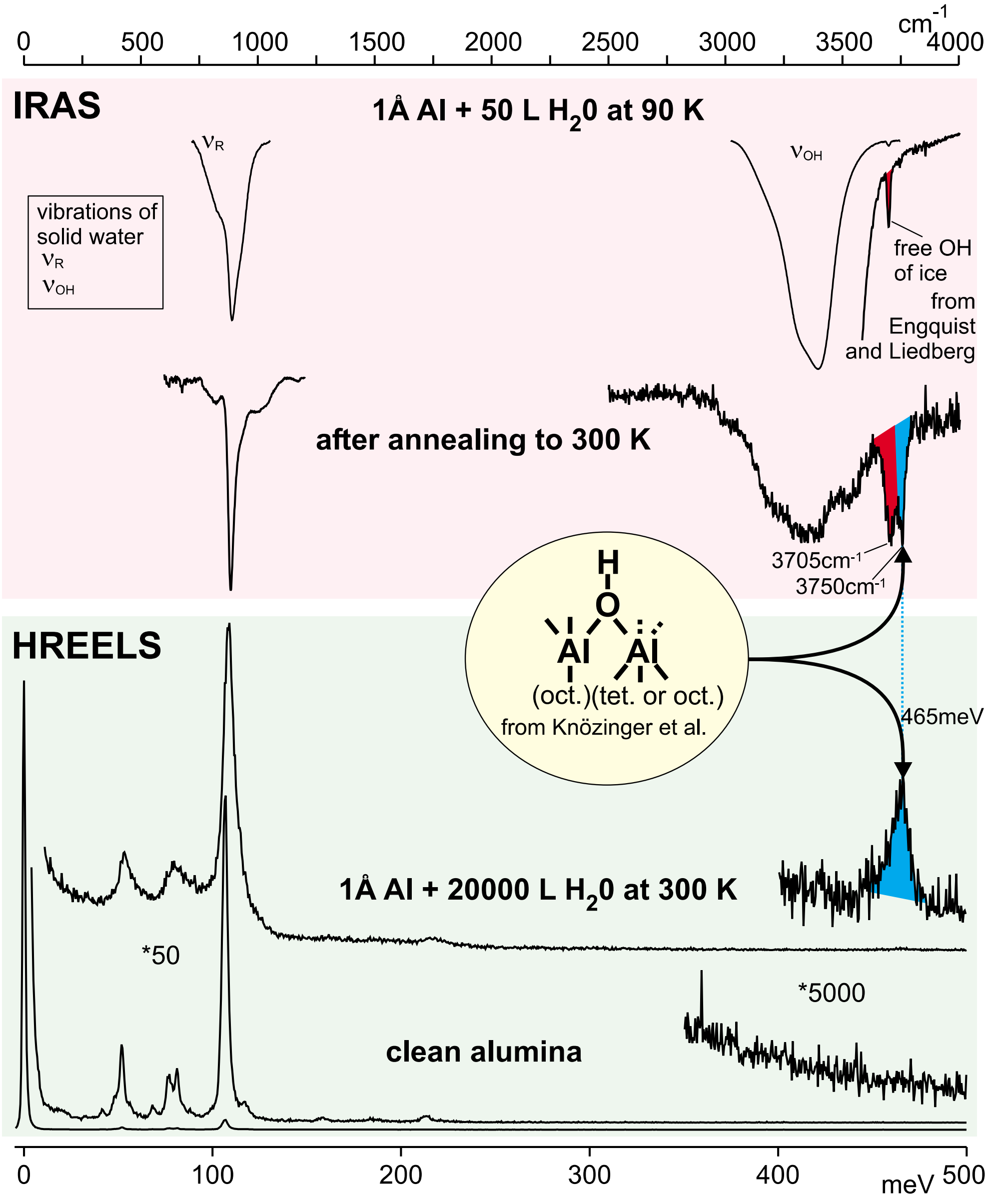

Fig. 7. Fourier transform IR spectra (IRAS) and electron energy loss spectra (HREELS) of a clean and an OH(+H_2O)-covered alumina film.

STM study from our laboratory. The upper left panel (a) shows the clean alumina surface as imaged by a scanning tunneling microscope [63]. The surface is well ordered and there are several kinds of defects on the surface. One of them are reflection domain boundaries between the two growth directions of $Al_2O_3(0001)$ on the NiAl(110) surface [48]. There are anti-phase domain boundaries within the reflection domains, and, in addition, there are point defects which are not resolved in the images. The image does not change dramatically after hydroxylating the film [45]. The

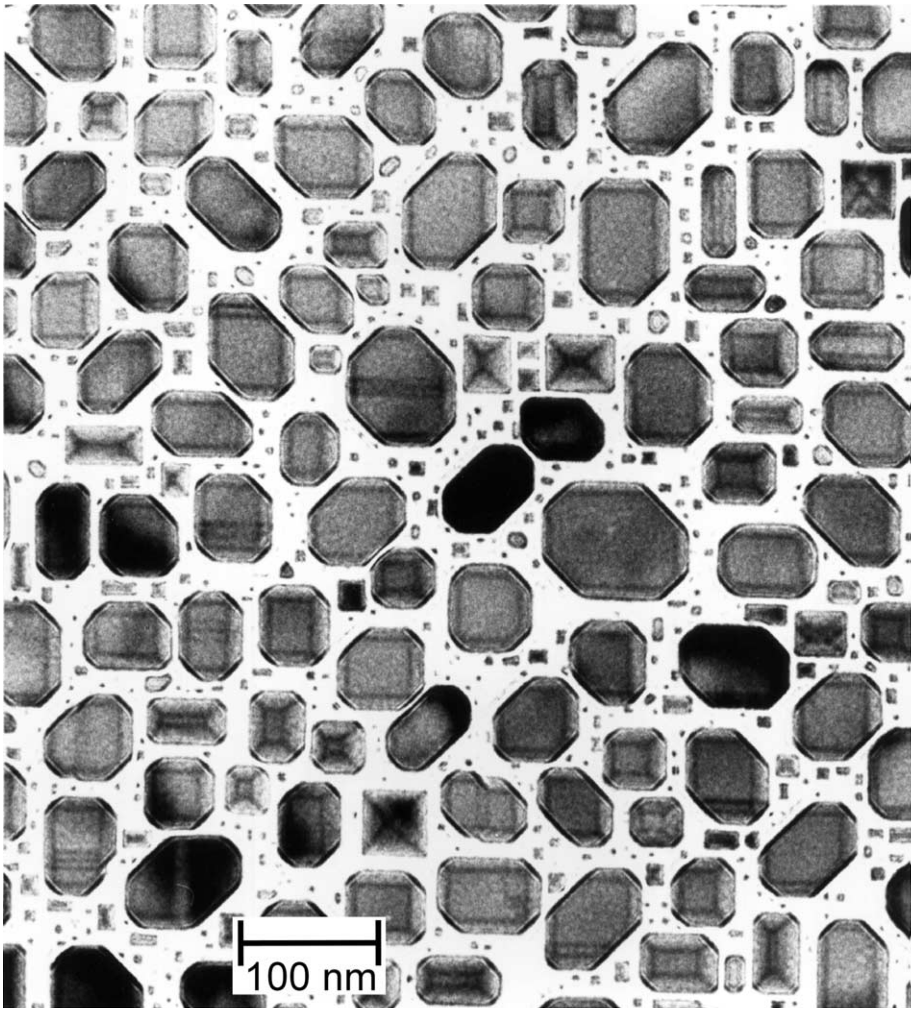

Fig. 8. Palladium nanocrystallites on MgO(1 0 0) as imaged via TEM [54].

additional panels show STM images of rhodium deposits on the clean surface at low temperature (b), and at room temperature (c) [64,65], as well as an image after deposition of Rh at room temperature on a hydroxylated substrate (d) [66]. The amount deposited onto the hydroxylated surface is equivalent to the amount deposited onto the clean alumina surface at room temperature. Upon vapor deposition of Rh at low temperature (the protrusions shown in Fig. 9b), small particles nucleate on the point defects of the substrate and a narrow distribution of sizes of particles is generated. If the deposition of Rh is performed at room temperature, the mobility of Rh atoms is considerably higher so that nucleation at the line defects of the substrate becomes dominant (features line up with the light lines in Fig. 9c). Consequently, all the material nucleates on steps, reflection domain and anti-phase domain boundaries. The particles have a relatively uniform size, in turn depending on the amount of material deposited. If the same amount of material is deposited onto a hydroxylated surface, the particles (the protrusions shown in Fig. 9d) are considerably smaller and distributed across the entire surface, i.e. a much higher metal dispersion is obtained [45].

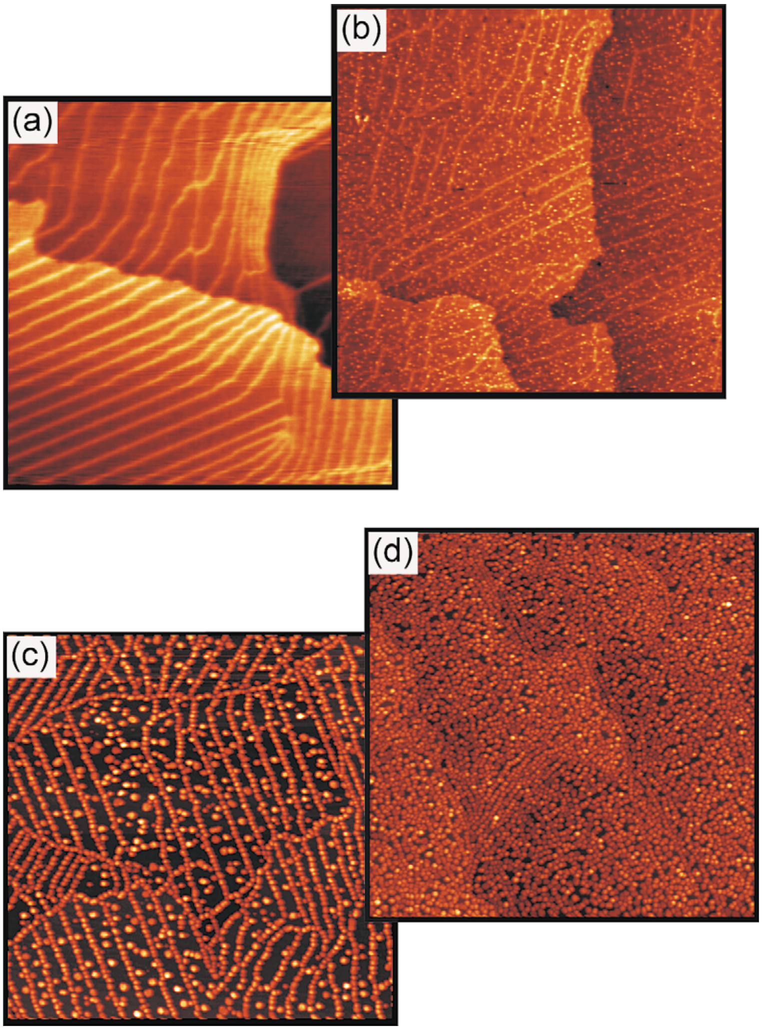

Fig. 9. Scanning tunneling images (3000 × 3000 Å^2, Al_2O_3/NiAl(1 1 0), $U_{tip} = 8$ V, $I = 0.8$ nA): (a) Clean alumina film, (b) after deposition of 0.1 Å of Rh at 90 K, (c) after deposition of 2 Å of Rh at 300 K, and (d) after deposition of 2 Å of Rh at 300 K on hydroxylated substrate onto the pre-hydroxylated alumina film.

The sintering process is an interesting subject. Research on this process is just beginning [64]. A more basic process is metal atom diffusion on oxide substrates.

Diffusion studies [67] could profit from atomic resolution, once it is obtained routinely for deposited aggregates on oxide surfaces. While for clean TiO_2 surfaces and a few other oxide substrates atomic resolution may be obtained routinely, there are few studies on deposited metal particles where atomic resolution has been reported [68]. An image of Pd metal clusters on MoS_2 is shown in Fig. 10a and exhibits 27 metal atoms in the cluster. A joint effort between Fleming Besenbacher and our group [69] has led to atomically resolved images of Pd aggregates deposited on a thin alumina film. Fig. 10b shows such an image of an aggregate of about 50 Å in width. The particle is crystalline and exposes on its top a (1 1 1) facet. Also, on the side, (1 1 1) facets, typical for a cuboctahedral particle, can be discerned.

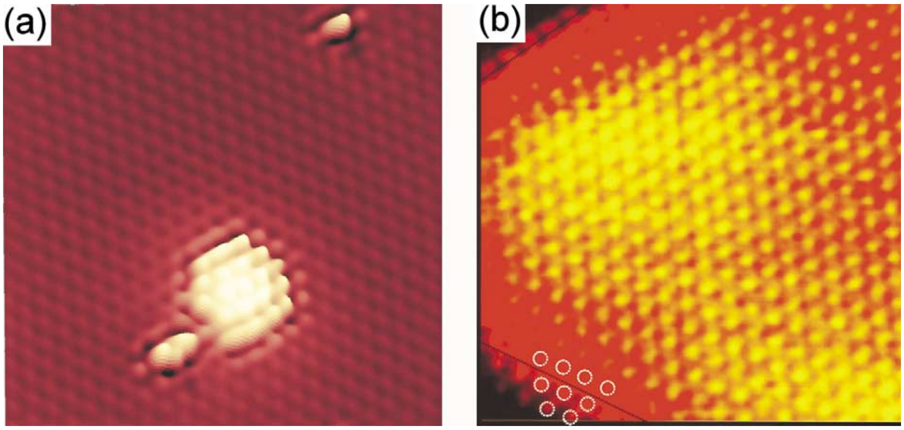

Fig. 10. Scanning tunneling image of: (a) an atomically resolved cluster of 27 Pd atoms arranged in two layers on a MoS_2 substrate [68], and (b) an atomically resolved Pd nanocrystallite grown on a thin alumina film [69].

While STM reveals the surface structure of deposited particles, their internal structure, in particular as a function of size, is not easily accessible through STM. In this connection, TEM studies on the same model systems help [70]. On the basis of numerous high resolution transmission electron microscopy (HRTEM) images, it has been possible to calculate the lattice constants as a function of particle size [70]. The corresponding plot is depicted in Fig. 11. It reveals that the atomic distances continuously decrease to 90% of the bulk value at a cluster size of 10 Å. On the other hand, the lattice constant approaches the Pt bulk value at a diameter of 30 Å. This effect also has been detected for Ta and Pd clusters on the thin alumina film, but seems to be less pronounced in these cases

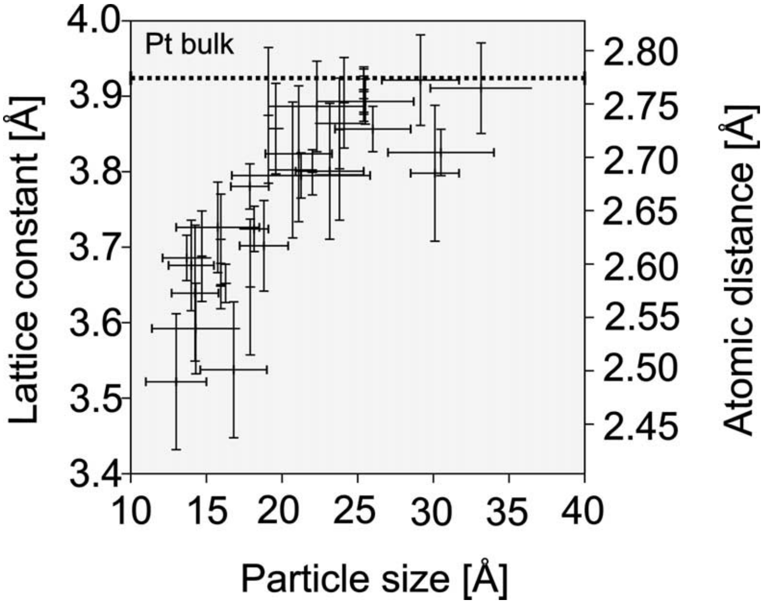

Fig. 11. Lattice constants and interatomic distances of Pt particles grown on Al_2O_3/NiAl(1 1 0) as a function of their size (the horizontal bars represent the difference of the widths and the lengths of the clusters, while the vertical bars are error bars).

[71,72]. Variations of interatomic distances as a function of particle size are known from calculations on isolated clusters and have occasionally been reported for deposits [73].

The deposits discussed so far were prepared with the intention to keep the size distribution narrow. The lateral distribution of aggregates on the surface, however, has not been an issue. If we consider reacting systems, interdiffusion of species between the particles, i.e. spillover processes, may become an important issue. Therefore, it may be desirable to control not only particle size and morphology but also interparticle distances. Based on electron beam lithography, Rupprechter et al. [74,75] have reported the preparation of two-dimensional arrays of Pt particles deposited onto amorphous SiO_2 layers. Particles of 25–40 nm average size could be produced as shown in Fig. 12. The image reveals an average height of 20 nm of these particles. In these studies [76–80] the average size is an order of magnitude larger than the particles imaged in Fig. 10.

The electronic structure of deposited metal aggregates reflects to a certain extent the geometric structure and vice versa.

Starting from an atomic level diagram, Fig. 13 shows how such a level diagram develops when more and more metal atoms agglomerate and finally form a solid with a periodic lattice. Upon formation of an aggregate from equivalent atoms, the atomic levels split into cluster orbitals. The splittings are characteristic of the interatomic interactions. Depending on the interaction strength, the split levels derived from a given atomic orbital start to energetically overlap with levels derived from other atomic orbitals. As long as the system has molecular character, there is an energy gap left between occupied and unoccupied levels. This is in contrast to the situation encountered for an infinite periodic metallic solid as presented on the right hand side of the figure, where no longer a gap between occupied and unoccupied levels exists. It is not hard to envision that, as we enlarge the number of atoms in an agglomerate, the gap between occupied and unoccupied orbitals effectively vanishes. This is the case if the energy gap decreases to a value close to the thermal energy in the system kT.

The question arises: How many atoms are necessary to induce a transition from an insulator to a metallic cluster? Reports in the literature claim numbers ranging from 20 to several hundred atoms in this respect [72,81–92]. One interesting extrapolation deduced from spectroscopic measurements of the gap of inorganic carbonyl cluster compounds containing a transition metal kernel and CO molecules as a ligand sphere as a function of the size of the metal kernel is shown in Fig. 14 [83]. It suggests that 70 atoms are sufficient to close the gap. A study from the author's laboratory on CO covered Pd and Rh clusters [86,92] yields a comparable value. In those cases where larger values have been obtained, the metals were Cu, Ag, Au, Al or alkali metals [81,82,93]. It is likely that the specific electronic structure of metals has an influence on the exact value.

Experiments on electronic structure so far have dealt with ensembles of clusters and relied upon the preparation of ensembles with narrow size distributions. Recording current–voltage curves in a scanning tunneling microscope for a given position (this procedure is called scanning tunneling spectroscopy), enables the investigation of single clusters, e.g., aggregates deposited on oxides [94]. Fig. 15 shows typical current–voltage curves for some aggregate sizes, i.e. Au on $TiO_2(110)$ [95]. While the large particles do not exhibit a plateau near $I = V = 0$, the smaller clusters do show the behavior expected for a system with a gap.

The electronic structure of deposited aggregates has also been probed via optical response [96–98]. Fig. 16 shows the optical absorption as well as the atomic force microscopy (AFM) image of an ensemble of small Ag clusters on mica [97]. The two absorption bands are associated with the optical excitation of a surface plasmon, i.e., a collective excitation of the electrons on a sphere, which corresponds to the so called Mie plasmon [6] mentioned in the introduction. There are two bands because the three possible oscillatory directions in a sphere no longer lead to the same plasmon energy for a free sphere deposited on a substrate. The oscillation perpendicular to the surface appears at higher energy than the two equal-energy oscillations within the surface plane [96]. This is illustrated in Fig. 17 where the dipole

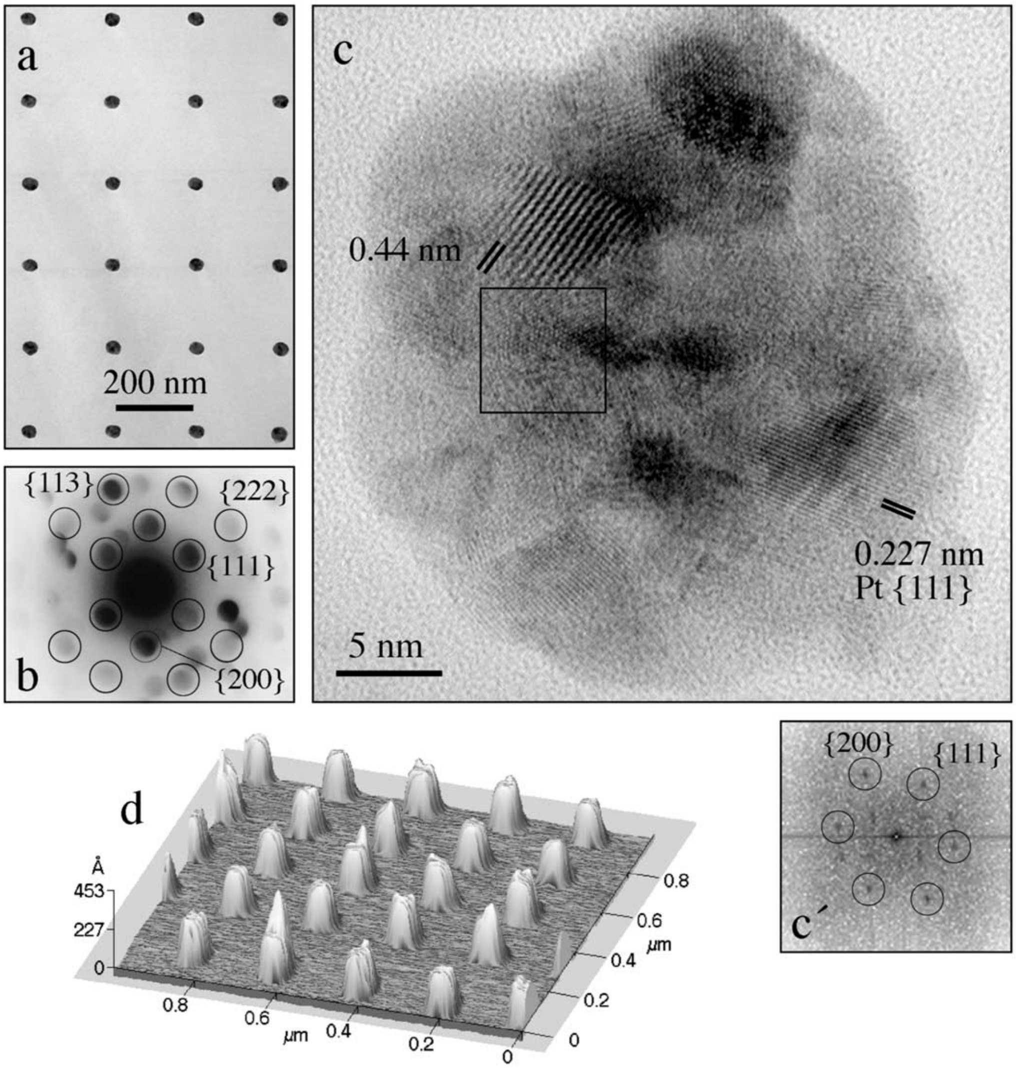

Fig. 12. (a) Transmission electron micrograph of a platinum nanoparticle array on SiO_2 (mean particle diameter 40 nm; interparticle distance 200 nm), (b) Microdiffraction pattern of an individual platinum particle showing its polycrystallinity (spots originating from a (1 1 0)-oriented crystalline grain within the polycrystalline platinum particle are marked by circles), (c) HRTEM micrograph and (c′) fast Fourier transform of a 25-nm platinum model catalyst particle. (d) AFM image of a platinum nanocluster array after several reaction-cleaning cycles [74].

in a sphere is indicated together with its image dipole in the substrate. The perpendicular dipoles couple to form a large dipole moment harder to excite (blue shift), while the parallel dipole couple to form a reduced dipole moment easier to excite (red shift). The widths of the bands depend on the size and the shape distributions of the clusters. Since there is a stronger variation in lateral shape than in height the blue shifted band is wider. The widths are therefore inhomogeneous, i.e., each cluster exhibits its own shift and the experiment measures the sum of these. Experiments on either a monodisperse cluster ensemble of single shape or experiments on individual clusters would be needed to investigate the homogeneous widths. Such experiments have been recently reported by using a

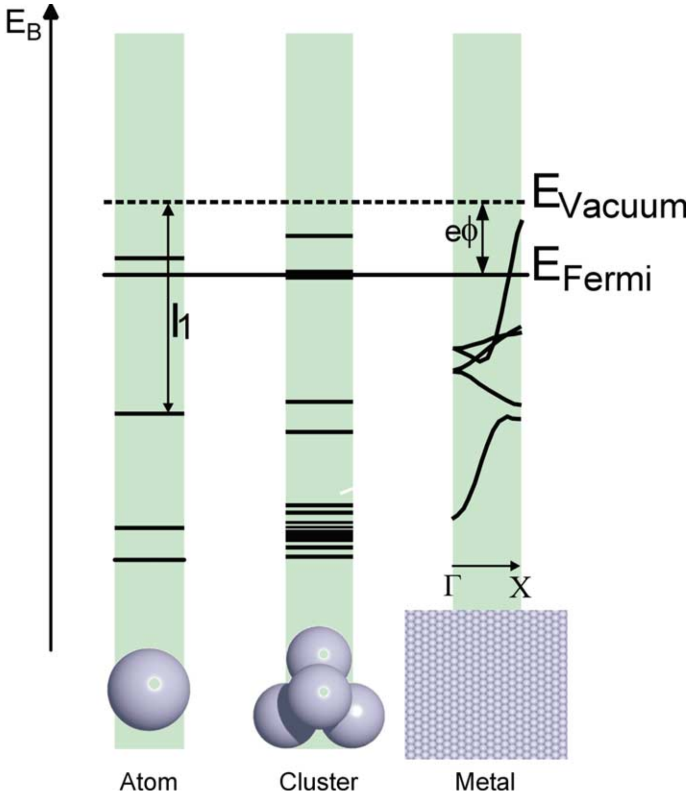

Fig. 13. Diagram illustrating the transition from an atom to a metal (E_B, binding energy; I_1, first ionization energy; e: electron charge; ϕ: work function; Γ, X: symmetry points in the Brillouin zone).

scanning tunneling device [99]. Schematically the setup is shown in Fig. 18a [100]. The tip is used to inject electrons into individual Ag clusters, in this case deposited on alumina for excitation. Then the light emitted from the clusters upon radiative decay is measured via a spectrometer outside the vacuum chamber. Fig. 18b shows the fluorescence spectra as a function of size referring to the specific clusters in the STM image, which occurs blurred because it was taken at high tunneling voltage necessary for excitation. A better representation of the size distribution of the Ag clusters is imaged in the second inset in Fig. 18b although even in this case one has to take account of the fact that due to tip convolution the actual size is considerably smaller than the imaged one. The peak shows a pronounced blue shift as a function of size consistent with observations on cluster ensembles of varying size. In this context it is interesting to look at the line widths of the resonance as a function of size. This is plotted in Fig. 18c. The line width is smallest for the larger clusters, i.e. 0.15 eV, and increases to 0.3 eV for the smallest ones studied. We consider this to be the homogeneous line width. The fact that it changes following an inverse cluster radius reveals the influence of the cluster surface becoming more important for smaller systems as a channel to deactivate the excited state through electron-surface scattering without generating radiation.

In the introduction we referred to the interaction of species from the gas phase with the deposited clusters. This is an important issue in catalysis as well as in understanding sensors.

An advantageous technique to expose a cluster to a gas and then re-establish ultrahigh vacuum is FTIR because it provides the resolution to differentiate between various adsorbed species. Again,

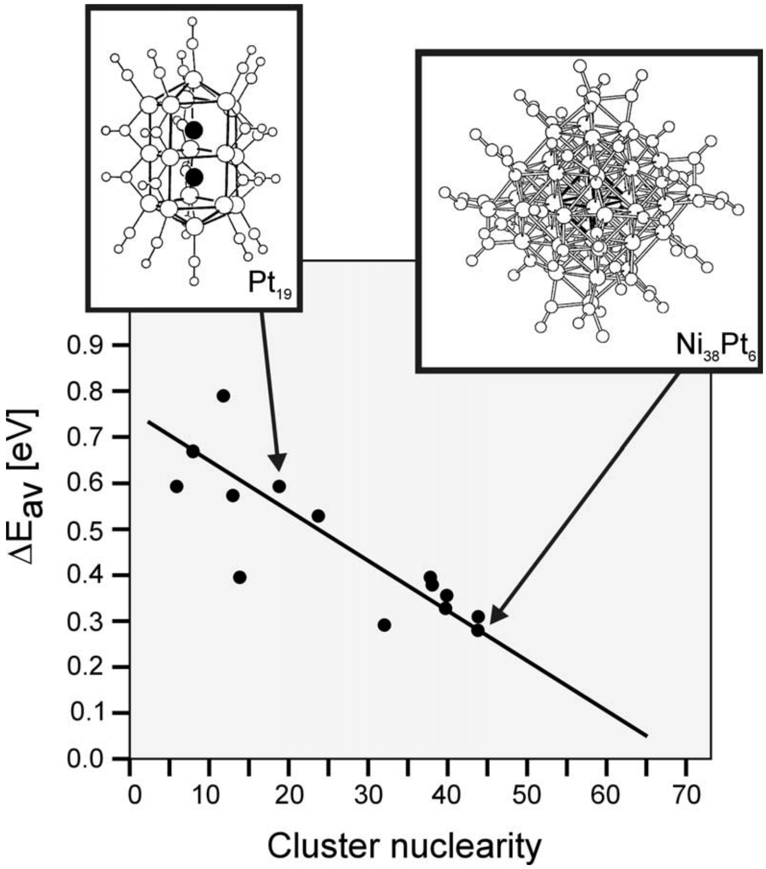

Fig. 14. Electronic excitation of lowest energy for several cluster compounds as a function of the number of metal atoms in the cluster (ΔE_{av} is the energy gap between occupied and unoccupied electronic states for cluster compounds). Reproduced with permission from de Biani et al. [83].

the thin film based systems are particularly well suited since the metallic support of the oxide films acts as a mirror at infrared frequencies. It is, however, also possible to perform such experiments on surfaces of bulk dielectrics as shown by the Hayden group [101,102].

Wayne Goodman and his group have published an interesting study of CO adsorption on Pd aggregates on Al_2O_3 films [94]. The results have been interpreted as characteristic for the adsorption of CO on different facets of the small crystalline aggregates. Although this interpretation does not take into account adsorption on the various defect sites of the aggregates [86], as pointed out in a more recent study [103], the data are indicative of the potential of this technique for the study of size dependent absorption phenomena. The presence of adsorbed molecules can change the morphology of deposited particles because in the presence of adsorbates molecular species may be found that detach themselves from a cluster and move across the surface. Such phenomena are interesting with respect to redispersing metal on a surface. For example, a catalyst could have been deactivated by cluster agglomeration. This process can be reversed to a certain extent by the formation of mobile species which can re-nucleate small metal particles when treated properly.

The infrared spectrum taken from a Rh deposit prepared and saturated with CO at 90 K is displayed in Fig. 19 (second spectrum) [104]. The most prominent feature in the stretching region of

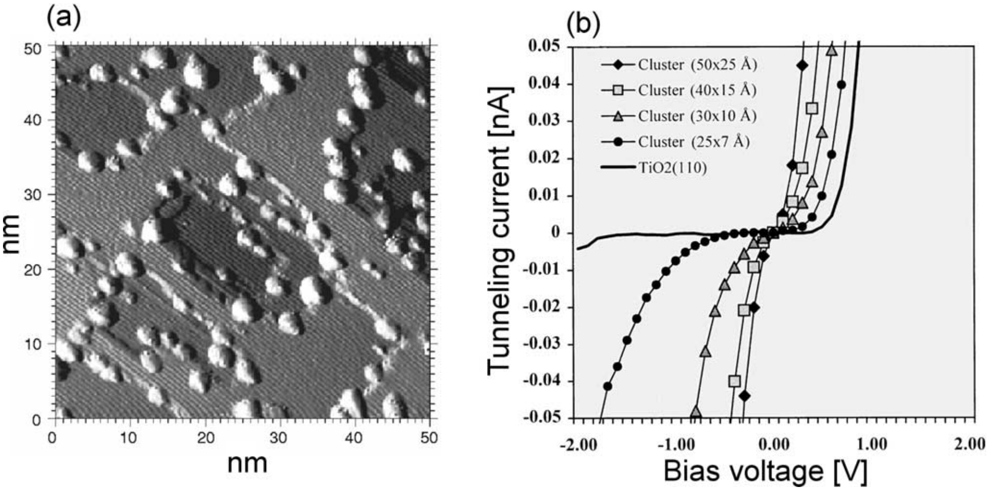

Fig. 15. Current–voltage (b) recorded for Au clusters of various sizes deposited onto a $TiO_2(1\,1\,0)$ surface. A typical STM picture of the system is shown in (a). (Adapted from Ref. [95].)

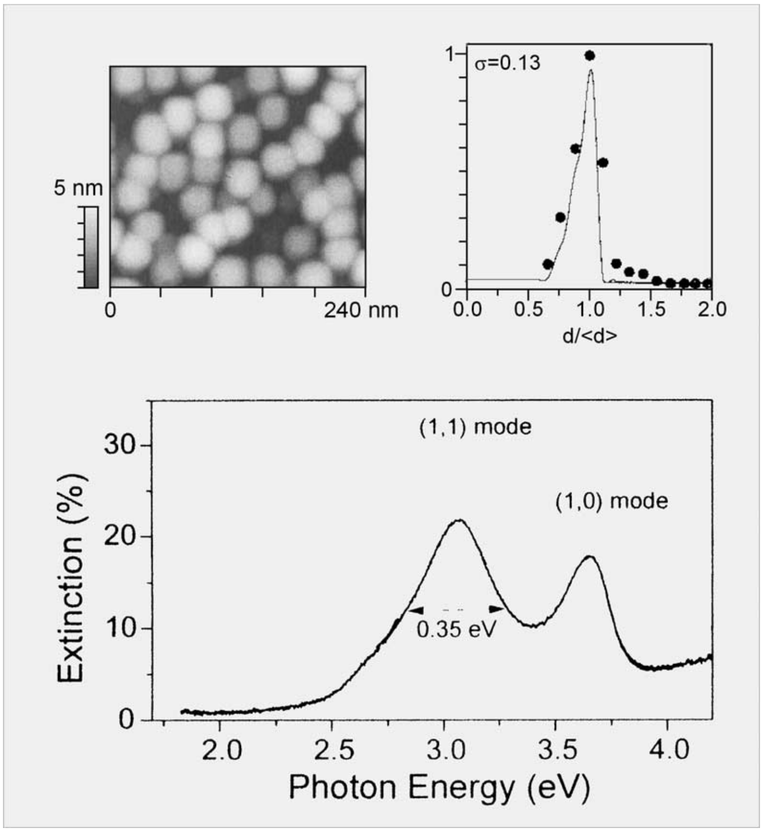

Fig. 16. Extinction spectra of small silver particles in the range of 2 eV $< E(\text{photon}) <$ 4 eV. The insets contain: (upper left panel) an AFM image of the particle distribution and (upper right panel) the normalized size distribution of the particles.

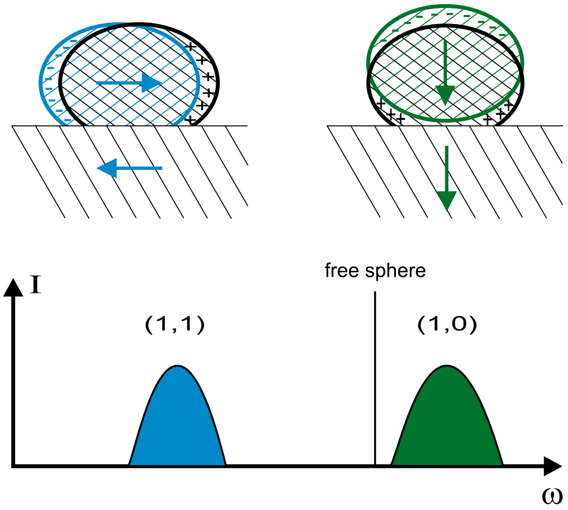

Fig. 17. Schematic representation of the surface plasmon excitations for ellipsoids attached to a solid substrate. The modes with parallel and perpendicular excitation dipole are indicated and the resulting spectrum is schematically indicated below.

terminally bonded CO molecules is a sharp, intense band at 2117 cm^{-1}. This signal has been shown to arise from isolated Rh atoms trapped at oxide defects [104]. While this species has been identified to be the geminal dicarbonyl ($Rh(CO)_2$), known to be the species involved in metal transport across the surface under reaction conditions, the nature of the defect site remained unclear. Features at lower frequencies have been assigned to molecules on Rh aggregates. In the top spectrum the feature of 2117 cm^{-1} is missing which means that a rhodium film deposited of 300 K does not contain isolated Rh atoms due to the higher mobility at this temperature. This established that $Rh(CO)_2$ sits in defect sites.

These studies on small Rh particles have been extended to neighboring elements in the periodic table. Infrared spectra recorded after deposition of comparable amounts of Pd, Rh, and Ir and subsequent CO saturation at 90 K are displayed in Fig. 20. We note differences in the low wave number region, where vibrational frequencies of molecules in multiply coordinated sites are found. As on single crystals, the CO population of such sites is highest on Pd [105,106], while no such CO is observed on Ir [107,108].

The differences in the region of terminally bonded CO, however, are much more pronounced. In the case of Ir, several distinct features are observed. In analogy to the $Rh(CO)_2$ band at 2117 cm^{-1}, the sharp signal at 2107 cm^{-1} has been attributed to $Ir(CO)_2$ species via isotopic mixture experiments (not shown). Bands with similar frequencies have been assigned to the symmetric stretch of $Ir^+(CO)_2$ on technical Ir/Al_2O_3 catalysts (2107–2090 cm^{-1}) [109] and on the iridium-loaded zeolite H-ZSM-5 (2104 cm^{-1}) [110]. The appearance of a number of bands at lower wave number is reminiscent of the 90 K Rh deposits (Fig. 20), pointing to a comparable nucleation behavior.

In contrast to that, no signs of atomically dispersed Pd or of structurally well-defined aggregates are observed. Indeed, the infrared spectrum is rather similar to that observed on much larger, disordered Pd aggregates [111]. At the same metal exposure, the Pd particles are found to be larger than the Rh aggregates by room temperature STM.

Infrared spectra of adsorbed CO thus provide valuable information on the size of metal nanoparticles, as long recognized in the catalysis related literature.

The literature contains several adsorption studies, (see for example [112]) employing other probe molecules such as hydrocarbons but in these cases reactions come into play which renders the situation even more complicated.

In recent years some progress has been made towards developing vibrational spectroscopy in the presence of a gas atmosphere. Two routes have been followed, one, the so called polarization modulated (PM-) FTIR method [113], and sum-frequency generation as the second one [114–116]. While the first is limited to flat substrates because it uses alignment and is a linear spectroscopy, the second one is generally applicable in principle but is a non-linear spectroscopy. In the latter case it is difficult to retrieve quantitative information but the method has the distinctive advantage of being sensitive only to the interface. For the above reasons it is difficult to apply PM-FTIR to cluster systems, while the applicability of the latter has just been demonstrated. On the basis of these methods one may study whether the ideas devel-

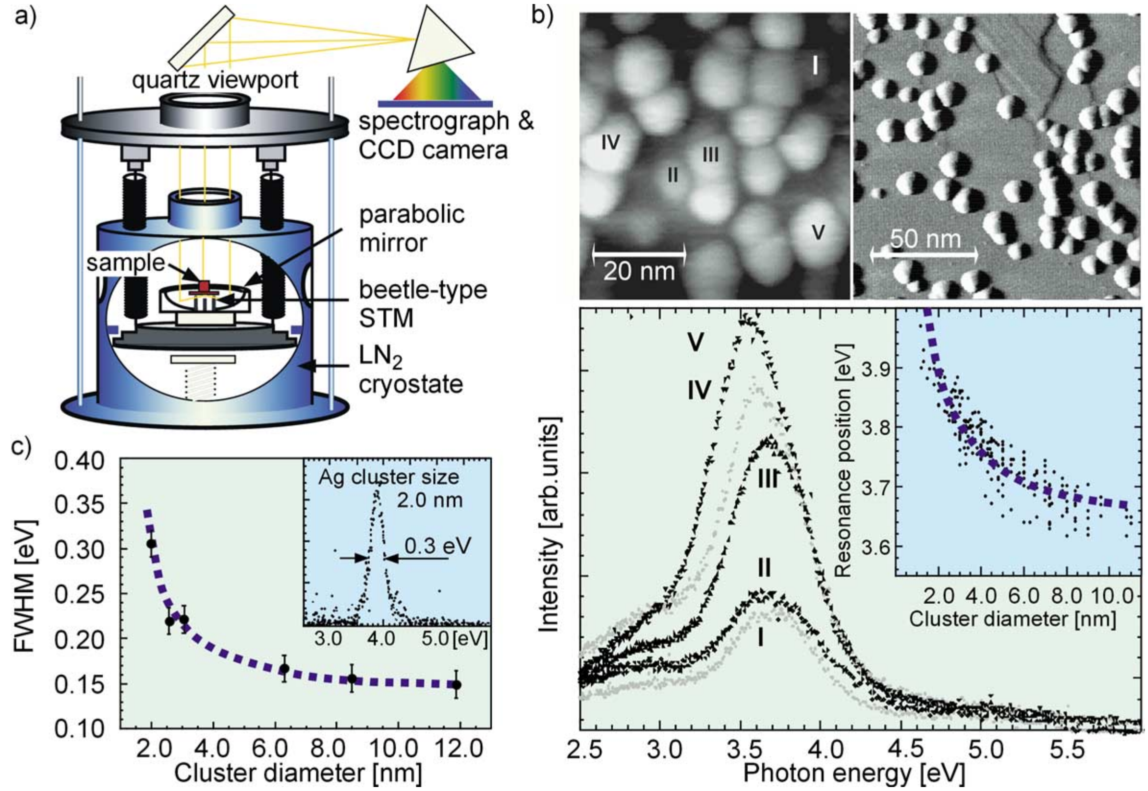

Fig. 18. (a) Schematic diagram of the experimental setup for the photon emission scanning tunneling microscope, (b) photon emission spectra as a function of particle size. The corresponding particles are marked in the upper left panel. The upper right panel shows a topological image of a typical cluster covered area. The size dependence of the resonance position of the plasmon excitation is shown in the inset on the left. (c) Line widths of the observed plasmon excitation as a function of particle size.

oped through studies under ultrahigh vacuum conditions can be extended to ambient pressures. Initial results look encouraging [116].

Vibrational spectroscopy on individual clusters has not been reported yet, but vibrational spectroscopy has been performed on carbon monoxide molecules bound to mass-selected deposited clusters. Heiz and coworkers [117–119] have mass selected in a quadrupole mass spectrometer Pt and Au clusters and deposited them onto a thin MgO film grown on a Mo substrate [13]. The assumption is that the clusters when deposited stay as deposited and the ensemble remains monodisperse. So far no one has demonstrated this by scanning probe microscopies although this should be possible. Fig. 21 shows FTIR spectra of CO adsorbed on mass-selectively deposited Pt_8 and Pt_{20} [119]. While the small Pt_8 cluster only exhibits bridging sites, the larger Pt_{20} cluster also shows a band typical for threefold hollow sites on Pt single crystals. An interesting result has been obtained on deposited Au clusters, which are, as mentioned before, also interesting research objects for low temperature CO oxidation. CO adsorbed on Au_8 clusters exhibit an infrared spectrum even at or above room temperature [120], indicating rather strong bonding. Fig. 21 contains the corresponding spectrum showing an unusually high CO stretching frequency. This is a result very different from CO adsorption on Au single crystal surfaces and larger Au particles [121]. The result could be important to understand why CO can be oxidized to CO_2 at very low temperature on gold catalysts!

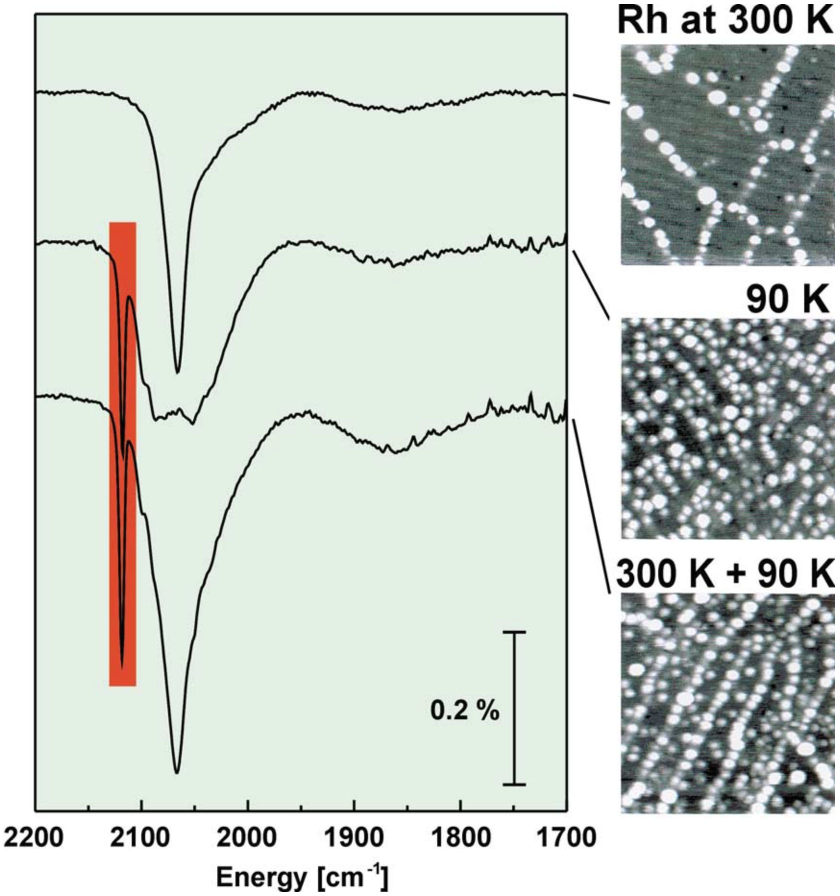

Fig. 19. Infrared spectra recorded after CO saturation of Rh deposits at 90 K, along with corresponding room temperature STM images (500 × 500 Å^2). Top: 0.057 ML Rh deposited at 300 K, middle: 0.057 ML Rh deposited at 90 K and bottom: 0.057 ML Rh deposited at 300 K, followed by the same exposure at 90 K.

The examples reviewed in this section indicate that cluster systems are complex and our knowledge on deposited clusters on insulating surfaces has increased enormously over the last ten years. Still we are only at the beginning of a crude understanding of the properties of aggregates and of the processes involved in their formation. There are many fascinating experiments one can think of that could be done on the basis of the knowledge so far accumulated. Some of these, which are to a large extent based on speculations, are considered in the next section in order to motivate more interest and activity in this field as suggested in the first line of the introduction.

3. Which are open questions and how could they be answered?

It is evident from the previous sections that the field is in its infancy and there are still many interesting questions unanswered. In the following we will examine a series of these questions and speculate about solutions and experiments to do. Even though we primarily discuss experimental aspects, the field can only develop and prosper through a concerted effort in experiment and theory. In particular the modern simulation methods are required to provide insight that cannot be gained through experiment alone.

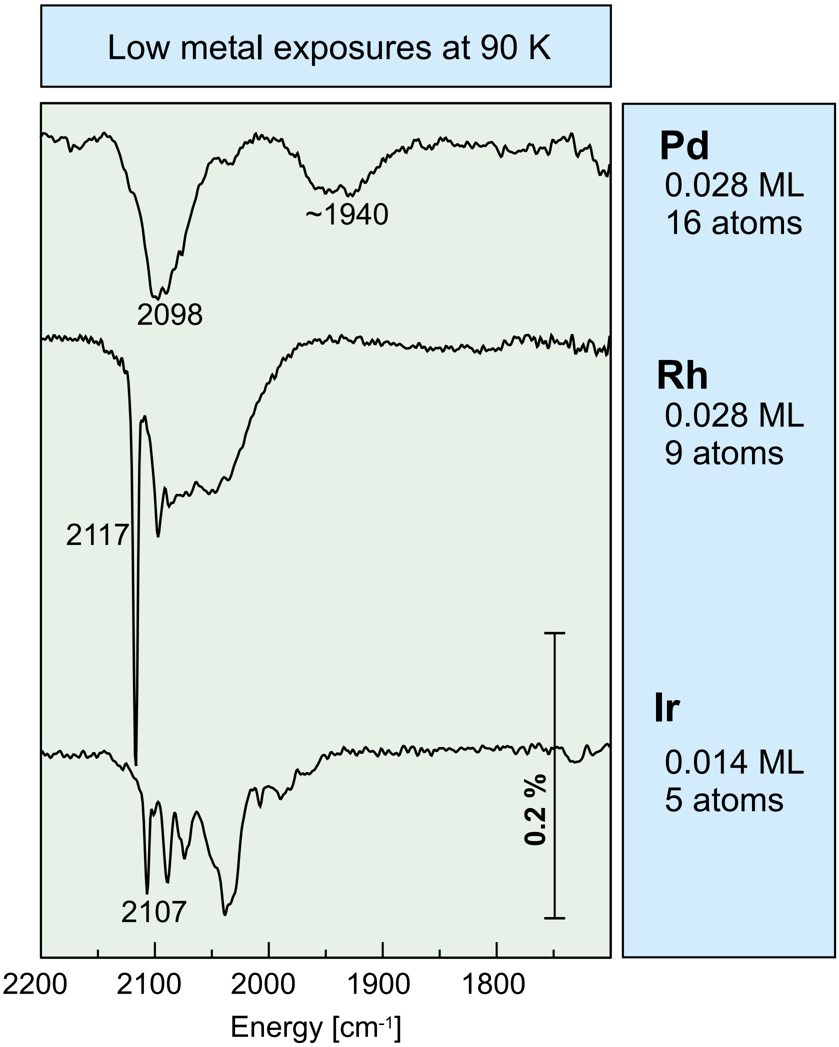

Fig. 20. Infrared spectra of Pd, Ir, and Rh deposited at 90 K and saturated with CO at the same temperature.

Before we become more specific let us identify areas of interest. Obvious ones are:

- Structure (geometric and electronic, including magnetic) at the atomic level of the metal particle–oxide interface under ambient conditions
- Control of structure and morphology
- Chemistry at the atomic level on the cluster
- Ultra fast dynamics and coherent control in and on clusters

There is information both on the oxide as the substrate as well as on the deposited metal particles. Although this may not yet be sufficient, there is very much less known on the metal particle–oxide interface [122]. Some of the important issues, however, are connected with this knowledge which renders the investigation of the metal particle–oxide interface an important one. Consider, as indicated in Fig. 22, a particle as an idealized cubo octahedron. Would it not be interesting to know whether the structure of the support underneath the particle is the same as the uncovered substrate? How is the electronic and geometric structure of the metal atoms in the aggregate in direct proximity to the substrate altered and how deep into the

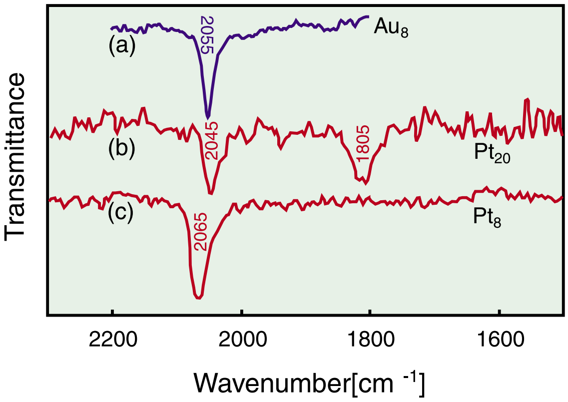

Fig. 21. Infrared spectra of CO covered mass-selective deposited Pt_8, Pt_{20} and Au_8 clusters on a thin MgO(100) film [119,120].

particle does this alteration reach? For example, has the particle sufficient metal character to screen the changes at the interface? Is the region at the circumference of the particle colored distinctively in Fig. 22, including metal particle and substrate atoms, characterized by particular electronic properties that could be of relevance for catalytic reactions? *Generally speaking, we would like to know the geometric structure of the entire deposited particle–substrate complex, and in addition the distribution of electrons within the system.* Can this information be obtained? The answer is: Very likely, if we assume that certain tools become available! Two experimental methods will be of central importance: electron microscopy [123], and X-ray structure determination with very intense light sources, such as synchrotrons [124] and in the future free electron laser (FEL) sources [125]. Other spectroscopic methods based on intense light sources, such as non-linear optical methods [126] could be applied using high energies in the UV, infrared, and possibly in the XUV regions. X-ray absorption [127] employing the high degree of linear and circular polarization of synchrotron light, as well as scanning probe microscopy can also play a role. Polarization dependent spectroscopic measurements provide key tests of electronic and magnetic structure [128].

In principle, electron microscopy can do a good part of the job! It allows the selection of an individual object in the sample, determines local

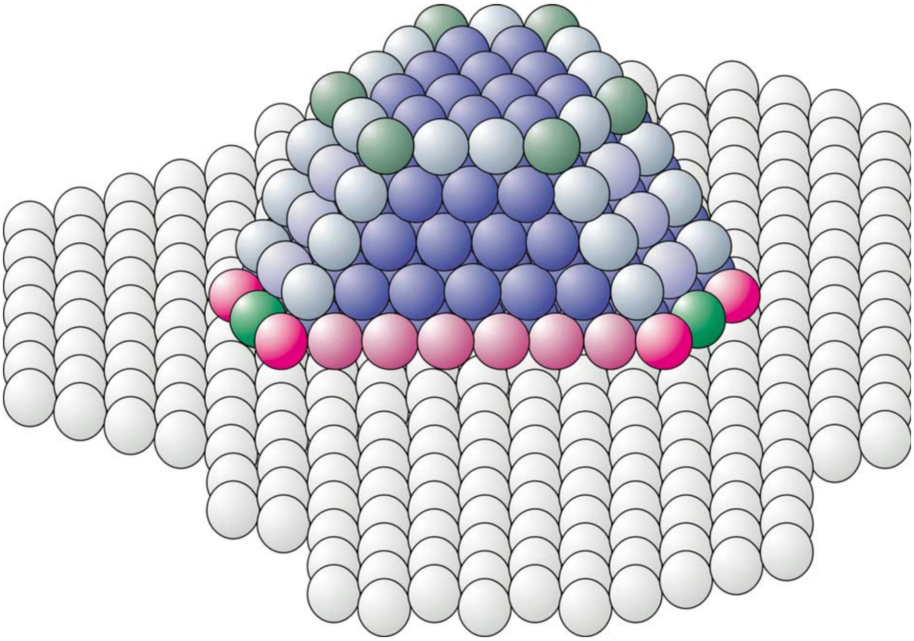

Fig. 22. Schematic representation of a cubo octahedral metal cluster on an insulating substrate. See also text. Chemically different sites on the cluster surface are colored differently.

structure with atomic resolution, and can be applied to cross-sectioned samples, so that we can image directly the interface. But: Electron microscopy is destructive, and is difficult to do under the influence of gases. It has chemical identification power, though limited, and may not be the method of choice to investigate electronic structure. Even today it is particularly difficult to image surfaces at atomic resolution with electron microscopy. For the purpose of surface imaging scanning probe microscopy is the method of choice. Photon based methods are by definition less destructive than electron based methods. Moreover, they can be used in the presence of a gas atmosphere, although care has to be exercised in this case as well. If it is possible to prepare uniform arrays of islands which are crystalline, —and some progress has already been demonstrated—then X-ray scattering and X-ray standing waves [129] are the promising tools to investigate the structure of deposited particles even under ambient conditions. If one had coherent X-rays from an X-ray laser [130] the investigation of structure and dynamics under ambient conditions would be in reach. With the advances recently made to shift the wavelength of coherent light into the XUV range by building free electron lasers, for example, the one at HASYLAB in Hamburg, a new generation of structure related experiments, including holography, would become available. The entire field of non-linear optical techniques, currently used in the lower frequency regimes could be applied at high energies opening up the possibility to selectively study interfaces similar to what is done at present in vibrational spectroscopy. These techniques could be used to study the metal particle–oxide interface. Photon based microscopy can benefit largely from the advent of high brilliance sources. There are several projects under way already to push the limits of lateral resolution to below 10 Å [131–133]. Also, X-ray optics is progressing with X-ray microscopy pushing the limits of resolution. In combinations with scanning probe microscopy, performed also under ambient conditions—a technology which is just being tested—experimental techniques would be available allowing us to answer the above question: Yes!

As has been indicated above, and alluded to on several occasions in the previous chapter, *it is of utmost importance to be able to control structure and morphology of cluster formation by understanding the elementary steps in the processes*, such as metal diffusion and aggregate migration on insulators. A good understanding of these processes would help to improve theoretical modeling studies. It is not known in detail how a single metal atom diffuses across an insulator surface. How does this process compare with metal-on-metal diffusion, where experimental studies have been successfully undertaken [134]? How does a cluster migrate on an oxide surface, and how does the concerted movement of atoms across the surface occur? Can a cluster dig itself into the substrate? Such questions need to be answered experimentally. The answers to these questions are intimately connected with knowing the real, i.e., defect-filled structure of the oxide substrate in the surface region. Scanning probe microscopy can play a decisive role in unraveling the number and distribution of such defect sites as well as their mobility. Whether these techniques, perhaps used in an inelastic tunneling mode, can be employed is an open question at present. It is conceivable to try to observe the vibrations at these local sites, similar to the observation of vibrational modes reported recently [135]. Definitely, photoelectron spectroscopy and vibrational spectroscopy are tools that can be used. The former can be combined with microscopy so that certain areas of the sample could be selected. Vibrations at such defects will have rather low frequencies so that traditional infrared techniques may be difficult to apply. There is certainly a chance for synchrotron based IR techniques [136]. If Raman spectroscopy could be developed into an even more sensitive technique to allow the study of species on single crystalline sample surfaces at low concentration, this would be an ideal tool [137,138]. There is also room for field ion microscopy since it has been shown to be applicable to study diffusion of individual metal atoms on oxide films.

Yet another aspect that has to be considered, when the area of structural control is discussed, is chemical modification of the substrate and self organization of the metal deposit. It is very important for the development of the field that preparative techniques are established, and tested. That the study of crystal growth remains a field of intense study to guarantee the availability of samples of highest quality. The examples discussed in the previous chapter illustrated how chemical modification can change the distribution, the sintering properties, and also the electronic structure of particles. This topic is at the heart of catalysis.

The third area addressed at the beginning of this chapter, namely how to study chemistry on clusters is another topic connected with of the examples mentioned in the introduction. Of course, again, of particular importance is this area for catalysis. *We would like to aim at a truly size dependent understanding of the chemistry on individual clusters.* This is meant in the broadest sense, namely understanding the making of a surface-to-atom or -molecule bond, breaking it, and reacting two species with each other, whereby the reaction may be triggered through thermal energy or other means, for example photochemically. Through a combination of tunneling microscopy and tunneling spectroscopy this is possible, and experiments are actually under way. There is no reason why the single molecule experiments via inelastic tunneling spectroscopy performed on single crystal metal surfaces could not be repeated on deposited clusters. By controlling the site of the molecule on the aggregate, i.e., on the terraces (Fig. 22), on the edges or on the corners one could study properties not only cluster specific but also site specific. In fact, it is to be expected that on small clusters edges or corners have a different influence than on large clusters, even if the overall symmetries are similar. It was demonstrated in the previous sections that the response of a cluster to light depends on the particle size. A consequence of this is that photochemistry depends on particle size, a fact that has already been demonstrated [139]. Still, however, there is a lot to be done in this area. While experiments on individual clusters have a certain appeal, experiments on ensembles of well defined size should not be forgotten. Molecular beam experiments can be decisive to provide quantitative information on kinetic parameters, so important in applications [140–142]. The big advantage is that all structural parameters are controlled simultaneously at the atomic level. In this arena the future has already begun.

One of the important questions in chemistry in general is: How does a molecular bond break [143–145]? This happens on the time scale of a molecular vibration, i.e., a picosecond. However, since energy dissipation via electron–electron interaction happens on the even shorter time scale of a few femtoseconds, *it is necessary to perform ultra fast spectroscopic experiments if we want to understand the dynamics of making and breaking of bonds on clusters at the atomic level.* Such experiments have been performed in the gas phase [146], and there are experiments on single crystal metal surfaces [147] but next to nothing is known for aggregates on insulating substrates. On the basis of what has been discussed we can expect that there are interesting size dependent effects. Again, the sample quality plays an important role to be able to perform ensemble averaging experiments. It is possible to probe such processes by performing photoelectron spectroscopy after absorption of two time delayed photons [147]. Here the photoelectron is emitted after absorption of two photons, whose pulse widths are of the order of femtoseconds. The delay between the absorption events of the photons can be chosen and varied, which in turn defines the time resolution. Since the detected particle is an electron photoelectron microscopy could be used to try to detect these processes even with spatial resolution. If it were possible to bring down the spatial resolution to the size of one cluster one could do ultra short experiments on individual clusters. Another route is to use an STM tip as an electron detector to bring down the spatial resolution [148]. In fact feasibility studies in this area are under way. In order to perform such experiments in the presence of a gas atmosphere electron based experiments may not be the optimal choice. Optical microscopy using ultra-small glass fiber tips to excite and/or record a spectrum (so-called scanning near field optical microscopy, SNOM), if developed further, may be an option, although it cannot be foreseen that with this method a single cluster can be selected out of a relatively dense cluster arrangement [149]. Usually, SNOM assumes that the investigated sample area contains only a few species. It is clear, however, that ultra fast spectroscopy combined with atomic resolution of reacting systems will be one of the most fascinating areas in chemical physics in these systems.

We have briefly discussed in the last section some open questions and strategies to possibly solve them. This catalogue of questions and answers can be extended almost infinitely. The specific areas touched here are considered to be opening up avenues to perform fascinating basic research that might be directly linked to applications.

4. Final remark

The attempt has been made to answer the simple question, why is the study of metal aggregates on oxides, described in this paper, an interesting subject. I have tried to put the field in a perspective that one can enter through applications from everyday life. The examples were chosen to document the current state of the art, and at the same time demonstrate that still a lot has to be achieved. In the third section we explore a whole variety of new, demanding experiments, which were chosen such, that in all likelihood they could be done given that the necessary tools are available and the scientific community receives continuous support, and, most importantly, there is a sufficient number of young talented scientists who are willing to take up a challenge.

Acknowledgements

This article has been written while I was staying as a chercheur associé at the Centre de Recherche sur les Mécanismes de la Croissance Cristalline (CRMC^2), a laboratory of CNRS in Luminy, France. I would like to thank my host, Claude Henry, for many fruitful discussions. Also I would like to thank the organizations sponsoring our research: Max-Planck-Society, Ministry of Education and Research of the Federal Republic of Germany, Deutsche Forschungsgemeinschaft, German Israeli Foundation, New Energy and Industrial Technology Development Organization (NEDO) of Japan, DAAD, Humboldt Foundation as well as Synetix (a member of the ICI group). I am indepted to my collaborators whose names appear in some of the references. For their help with this article I would like to thank Heiko Hamann, Yvonne Gründer, and Helmut Kuhlenbeck.

References

[1] G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 4, Wiley-VCH Verlagsgesellschaft mbH, Weinheim, 1997.

[2] Sensors update H. Baltes, W. Gospel, J. Hesse (Eds.), Sensor Technology Applications—Markets, vol. 1, VCH Verlagsgesellschaft mbH, Weinheim, 1996.

[3] H. Ulmer, J. Mitrovics, G. Noetzel, U. Weimar, W. Goepel, Odours and flavours identified with hybrid modular sensor systems, Sens. Actuators B 43 (1997) 24.

[4] I. Lundstroem, Why bother about gas-sensitive field-effect devices? Sens. Actuators A 56 (1996) 75.

[5] First Toyota Workshop on Magnetism and Magnetic Materials for High Density Information Storage, Toyota Institute of Technology, 1997; in J. Magn. Magn. Mater., vol. 175, Elsevier, Brussels, Belgium.

[6] A. Mie, Beiträge zur optik trüber medien, speziell kolloidaler metalllösungen, Ann. Phys. 25 (1908) 377.

[7] P. Chakraborty, Metal nanoclusters in glasses as nonlinear photonic materials, J. Mat. Sci. 33 (1998) 2235.

[8] H.-J. Freund, E. Umbach (Eds.), Adsorption on Ordered Surfaces of Ionic Solids and Thin Films, Springer Series in Surface Sciences, vol. 33, Springer, Heidelberg, 1993.

[9] G.H. Vurens, M. Salmeron, G.A. Somorjai, The preparation of thin ordered transition metal oxide films on metal single crystals for surface science studies, Progr. Surf. Sci. 32 (1989) 333.

[10] V.E. Henrich, P.A. Cox, The Surface Science of Metal Oxides, Cambridge University Press, Cambridge, 1994.

[11] H.-J. Freund, H. Kuhlenbeck, V. Staemmler, Oxide surfaces, Rep. Progr. Phys. 59 (1996) 283, Review.

[12] H.-J. Freund, Adsorption of gases on complex solid surfaces, Angew. Chem. Int. Ed. Engl. 36 (1997) 452, Review.

[13] D.W. Goodman, Model catalysts—from extended single crystals to supported particles, Surf. Rev. Lett. 2 (1995) 9.

[14] P.L.J. Gunter, J.W.H. Niemantsverdriet, F.H. Ribeiro, G.A. Somorjai, Surface science approach to modeling supported catalysts, Catal. Rev. Sci. Eng. 39 (1997) 77.

[15] D.A. Bonnell, Scanning tunneling microscopy and spectroscopy of oxide surfaces, Progr. Surf. Sci. 57 (1998) 187.

[16] U. Diebold, J.F. Anderson, K.-O. Ng, D. Vanderbilt, Evidence for the tunneling site on transition-metal oxides: $TiO_2(110)$, Phys. Rev. Lett. 77 (1996) 1322.

[17] P.W. Murray, F.M. Leibsle, C.A. Muryn, H.J. Fisher, C.F.J. Flipse, G. Thornton, Interrelationship of structural

elements on $TiO_2(100)$-(1 × 3), Phys. Rev. Lett. 72 (1994) 689.

[18] P.W. Murray, N.G. Condon, G. Thornton, Effect of stoichiometry on the structure of $TiO_2(110)$, Phys. Rev. B 51 (1995) 10989.

[19] H. Onishi, Y. Iwasawa, Reconstruction of $TiO_2(110)$ surface: STM study with atomic-scale resolution, Surf. Sci. 313 (1994) L783.

[20] H. Onishi, Y. Iwasawa, STM-imaging of formate intermediates adsorbed on a $TiO_2(110)$ surface, Chem. Phys. Lett. 226 (1994) 111.

[21] H. Onishi, K. Fukui, Y. Iwasawa, Atomic-scale surface structures of $TiO_2(110)$ determined by scanning tunneling microscopy—a new surface-limited phase of titanium oxide, Bull. Chem. Soc. Jpn. 68 (1995) 2447.

[22] H. Onishi, Y. Iwasawa, Dynamic visualization of a metal-oxide-surface/gas-phase reaction: time-resolved observation by scanning tunneling microscopy at 800 K, Phys. Rev. Lett. 76 (1996) 791.

[23] G. Charlton, P.B. Howes, C.L. Nicklin, P. Steadman, J.S.G. Taylor, C.A. Muryn, S.P. Harte, J. Mercer, R. McGrath, D. Norman, T.S. Turner, G. Thornton, Relaxation of $TiO_2(110)$-(1 × 1) using surface X-ray diffraction, Phys. Rev. Lett. 78 (1997) 495.

[24] G. Renaud, Oxide surfaces and metal/oxide interfaces studied by grazing incidence X-ray scattering, Surf. Sci. Rep. 32 (1998) 1.

[25] P.W. Tasker, Adv. Ceram. 10 (1984) 176.

[26] W.C. Mackrodt, R.J. Davey, S.N. Black, R. Docherty, The morphology of α-Al_2O_3 and α-Fe_2O_3: the importance of surface relaxation, J. Cryst. Growth 80 (1987) 441.

[27] C. Noguera, Physics and Chemistry at Oxide Surfaces, Cambridge University Press, Cambridge, 1996.

[28] H. Over, Y.D. Kim, A.P. Seitsonen, S. Wendt, E. Lundgren, M. Schmid, P. Varga, A. Morgante, G. Ertl, Atomic-scale structure and catalytic reactivity of the $RuO_2(110)$ surface, Science 287 (2000) 1474.

[29] Y.D. Kim, A.P. Seitsonen, M. Schwegmann, H. Over, Epitaxial Growth of $RuO_2(100)$ on Ru(1 0 −1 0): Surface Structure and Other Properties, J. Phys. Chem. B 105 (2001) 2205–2211.

[30] P. Guénard, G. Renaud, A. Barbier, M. Gautier-Soyer, Determination of the α-$Al_2O_3(0001)$ surface relaxation and termination by measurements of crystal truncation rods, Surf. Rev. Lett. 5 (1998) 321.

[31] F. Rohr, M. Bäumer, H.-J. Freund, J.A. Mejias, V. Staemmler, S. Müller, L. Hammer, K. Heinz, Strong relaxations the $Cr_2O_3(0001)$ surface as determined via low-energy electron diffraction and molecular dynamics simulations, Surf. Sci. 372 (1997) L291.

[32] F. Rohr, M. Bäumer, H.-J. Freund, J.A. Mejias, V. Staemmler, S. Müller, L. Hammer, K. Heinz, Erratum: Strong relaxations a the $Cr_2O_3(0001)$ surface as determined via low-energy electron diffraction and molecular dynamics simulations, Surf. Sci. 372 (1997) L291, Surf. Sci. 389 (1997) 391.

[33] W. Weiss, Structure and composition of thin epitaxial iron oxide films grown onto Pt(1 1 1), Surf. Sci. 377–379 (1997) 943.

[34] I. Manassidis, A. De Vita, M.J. Gillan, Structure of the (0 0 0 1) surface of α-Al_2O_3 from first principles calculations, Surf. Sci. 285 (1993) L517.

[35] I. Manassidis, M.J. Gillan, Structure and energetics of alumina surfaces calculated from first principles, J. Am. Ceram. Soc. 77 (1994) 335.

[36] C. Rehbein, N.M. Harrison, A. Wander, The structure of the α-$Cr_2O_3(0001)$ surface: an ab initio total energy study, Phys. Rev. B 54 (1996) 14066.

[37] X.-G. Wang, W. Weiss, S.K. Shaikhoutdinov, M. Ritter, M. Petersen, F. Wagner, R. Schlögl, M. Scheffler, The hematite α-Fe2O3(0 0 0 1) surface: evidence for domains of distinct chemistry, Phys. Rev. Lett. 81 (1998) 1038.

[38] K. Heinz, Geometrical and chemical restructuring of clean metal surfaces as retrieved by LEED, Surf. Sci. 299–300 (1994) 433.

[39] N.M. Harrison, X.-G. Wang, J. Muscat, M. Scheffler, The influence of soft vibrational modes on our understanding of oxide surface structure, Faraday Disc. 114 (1999) 305.

[40] H. Schmalzried, Chemical Kinetics of Solids, Verlag Chemie, Weinheim, 1995.

[41] J.G. Fripiat, A.A. Lucas, J.M. André, E.G. Derouane, On the stability of polar surface planes of macroscopic ionic crystals, Chem. Phys. 21 (1977) 101.

[42] D. Cappus, C. Xu, D. Ehrlich, B. Dillmann, C.A. Ventrice Jr., K. Al-Shamery, H. Kuhlenbeck, H.-J. Freund, Hydroxyl groups on oxide surfaces: NiO(1 0 0), NiO(1 1 1), and $Cr_2O_3(111)$, Chem. Phys 177 (1993) 533.

[43] F. Rohr, K. Wirth, J. Libuda, D. Cappus, M. Bäumer, H.-J. Freund, Hydroxyl driven reconstruction of the polar NiO(1 1 1) surface, Surf. Sci. 315 (1994) L977.

[44] X.-G. Wang, A. Chaka, M. Scheffler, Effect of the environment on α-$Al_2O_3(0001)$, Phys. Rev. Lett. 84 (2000) 3650.

[45] J. Libuda, M. Frank, A. Sandell, S. Andersson, P.A. Brühwiler, M. Bäumer, N. Mårtensson, H.-J. Freund, Interaction of rhodium with hydroxylated alumina model substrates, Surf. Sci. 384 (1997) 106.

[46] M. Heemeier, M. Frank, J. Libuda, K. Wolter, H. Kuhlenbeck, M. Bäumer, H.-J. Freund, The influence of OH groups on the growth of Rhodium on alumina: a model study, Catal. Lett. 68 (2000) 19.

[47] M.M. Ivey, H.C. Allen, A. Avoyan, K.A. Martin, J.C. Hemminger, Dimerization of 1,3-butadiene on highly characterized hydroxylated surfaces of ultrathin films of gamma-Al_2O_3, J. Am. Chem. Soc. 120 (42) (1998) 10980.

[48] R.M. Jaeger, H. Kuhlenbeck, H.-J. Freund, M. Wuttig, W. Hoffmann, R. Franchy, H. Ibach, Formation of a well-ordered aluminium oxide overlayer by oxidation of NiA(1 1 0), Surf. Sci. 259 (1991) 235.

[49] I. Engquist, B. Liedberg, D_2O ice on controlled wettability selfassembled alkanethiolate monolayers—Cluster formation and substrate–adsorbate interaction, J. Phys. Chem. 100 (1996) 20089.

[50] H. Knözinger, P. Ratnasamy, Catalytic aluminas: surface models and characterization of surface sites, Catal. Rev. Sci. Eng. 17 (1978) 31.

[51] C.B. Duke (Ed.), Surface Science: The First Thirty Years, vol. 299/300, Elsevier, Amsterdam, 1994.

[52] H. Poppa, Nucleation growth, and, TEM analysis of metal particles and clusters deposited in UHV, Catal. Rev. Sci. Eng. 35 (1993) 359.

[53] C.R. Henry, Surface studies of supported model catalysts, Surf. Sci. Rep. 31 (1998) 231.

[54] C. Goyhenex, C.R. Henry, J. Urban, In-situ measurements of the lattice parameter of supported palladium clusters, Phil. Mag. A 69 (1994) 1073.

[55] M.-C. Wu, P.J. Møller, Studies of the electronic structure of, Surf. Sci. 224 (1989) 250.

[56] P.J. Møller, M.-C. Wu, Surface geometrical structure and incommensurate growth: ultrathin Cu films on $TiO_2(110)$, Surf. Sci. 224 (1989) 265.

[57] M.C. Wu, P.J. Møller, Direct and substrate-phonon-assisted electronic transitions in $Cu/TiO_2(110)$ observed by AREELS, Surf. Sci. 235 (1990) 228.

[58] P.J. Møller, J. Nerlov, Ultrathin films of Cu on $ZnO(11-20)$: growth and electronic structure, Surf. Sci. 307–309 (1993) 591.

[59] P.W. Murray, J. Shen, N.G. Condon, S.J. Pang, G. Thornton, STM study of PD growth on $TiO_2(100)$-(1×3), Surf. Sci. 380 (1997) L455.

[60] P. Stone, R.A. Bennett, M. Bowker, Reactive re-oxidation of reduced $TiO_2(110)$ surfaces demonstrated by high temperature STM movies, New J. Phys. 1 (1998–99) 8.

[61] U. Diebold, Structure(s) and reactivity of the $TiO_2(110)$ surface, Proc. of 1st Int. Workshop on Oxide Surfaces, Elmau, Germany 1999.

[62] C.T. Campbell, Ultrathin metal films and particles on oxide surfaces: structural, electronic and chemisorption properties, Surf. Sci. Rep. 27 (1997) 1.

[63] J. Libuda, F. Winkelmann, M. Bäumer, H.-J. Freund, T. Bertrams, H. Neddermeyer, K. Müller, Structure and defects of an ordered alumina film on NiAl(110), Surf. Sci. 318 (1994) 61.

[64] M. Bäumer, H.-J. Freund, Metal deposits on well-ordered oxide films, Progr. Surf. Sci. 61 (1999) 127.

[65] S. Stempel, M. Bäumer, H.-J. Freund, STM studies of rhodium deposits on an ordered alumina film—resolution and tip effects, Surf. Sci. 402–404 (1998) 424.

[66] M. Heemeier, Ph.D. thesis, Freie Universität Berlin, in preparation.

[67] N. Ernst, B. Duncombe, G. Bozdech, M. Naschitzki, H.-J. Freund, Field ion microscopy of platinum adatoms deposited on a thin Al_2O_3 film on NiAl(110), Ultramicroscopy 79 (1999) 231.

[68] A. Piednoir, E. Perrot, S. Granjeaud, A. Humbert, C. Chapon, C.R. Henry, Atomic resolution on small three-dimensional metal clusters by STM, Surf. Sci. 391 (1997) 19.

[69] K.H. Hansen, T. Worren, S. Stempel, E. Lægsgaard, M. Bäumer, H.-J. Freund, F. Besenbacher, I. Stensgaard, Palladium nanocrystals on Al_2O_3: structure and adhesion energy, Phys. Rev. Lett. 83 (1999) 4120.

[70] M. Klimenkov, S. Nepijko, H. Kuhlenbeck, M. Bäumer, R. Schlögl, H.-J. Freund, The structure of Pt-aggregates on a supported thin aluminum oxide film in comparison with unsupported alumina—a transmission electron microscopy study, Surf. Sci. 391 (1997) 27.

[71] S.A. Nepijko, M. Klimenkov, H. Kuhlenbeck, D. Zemlyanov, D. Herein, R. Schlögl, H.-J. Freund, TEM study of tantalum clusters on Al_2O_3/NiAl(110), Surf. Sci. 412/413 (1998) 192.

[72] S.A. Nepijko, M. Klimenkov, M. Adelt, H. Kuhlenbeck, R. Schlögl, H.-J. Freund, Structural investigation of palladium clusters on γ-$Al_2O_3(111)$/NiAl(110) with transmission electron microscopy, Langmuir 15 (1999) 5309.

[73] C. Solliard, M. Flueli, Surface stress and size effect on the lattice parameter in small particles of gold and platinum, Surf. Sci. 156 (1985) 487.

[74] G. Rupprechter, A.S. Eppler, G.A. Somorjai, A new model catalyst studied by HREM and AFM: Platinum nanoparticle arrays on silica fabricated by electron beam lithography, in: H.A.C. Benavides, M.J. Yacamàn (Eds.), Electron Microscopy, vol. II, Institute of Physics Publishing, Bristol, 1998, p. 369.

[75] A.S. Eppler, G. Rupprechter, L. Guczi, G.A. Somorjai, Model catalysts fabricated using electron beam lithography and pulsed laser deposition, J. Phys. Chem. B 101 (1997) 9973.

[76] K. Wong, S. Johansson, B. Kasemo, Nanofabricated model catalysts, Faraday Disc. 105 (1996) 237.

[77] P.W. Jacobs, F.H. Ribeiro, G.A. Somorjai, S.J. Wind, New model catalysts—uniform platinum cluster arrays produced by electron beam lithography, Catal. Lett. 37 (1996) 131.

[78] W. Gotschy, K. Vonmetz, A. Leitner, F.R. Aussenegg, Thin films by regular patterns of metal nanoparticles—tailoring the optical properties by nanodesign, Appl. Phys. B. Laser and Optics 63 (1996) 381.

[79] F. Cerrina, C. Marrian, A path to nanolithography, MRS Bull. 21 (1996) 56.

[80] P.B. Fischer, S.Y. Chou, 10 nm electron beam lithography and sub-50 nm overlay using a modified scanning electron microscope, Appl. Phys. Lett. 62 (1993) 2989.

[81] G. Schmid (Ed.), Clusters and Colloids From Theory to Applications, VCH Verlagsgesellschaft mbH, Weinheim, 1994.

[82] W. Ekardt, Metal Clusters, Wiley, Chichester, 1999.

[83] F.F. deBiani, C. Femoni, M.C. Iapalucci, G. Longoni, P. Zanello, A. Ceriotti, Redox behavior of $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n = 4$–6) anions: a series of metal carbonyl clusters displaying electron-sink features, Inorg. Chem. 38 (1999) 3721.

[84] B.F.G. Johnson, Transition Metal Clusters, Wiley, Chichester, 1980.

[85] G.K. Wertheim, S.B. DiCenzo, D.N.E. Buchanan, Noble and transition metal clusters: the d bands of silver and palladium, Phys. Rev. B 33 (1986) 5384.

[86] A. Sandell, J. Libuda, P. Brühwiler, S. Andersson, A. Maxwell, M. Bäumer, N. Mårtensson, H.-J. Freund, Electron spectroscopy studies of small deposited metal particles, J. Electron Spectrosc. Rel. Phenom. 76 (1995) 301.

[87] R. Unwin, A.M. Bradshaw, Photoelectron spectroscopy of palladium particle arrays on a carbon substrate, Chem. Phys. Lett. 58 (1978) 58.

[88] G.K. Wertheim, Electronic structure of metal clusters, Z. Phys. D 12 (1989) 319.

[89] S.-T. Lee, G. Apai, M.G. Mason, R. Benbow, Z. Hurych, Evolution of band structure in gold clusters as studied by photoemission, Phys. Rev. B 23 (1981) 505.

[90] V. De Gouveia, B. Bellamy, Y. Hadj Romdhane, A. Mason, M. Che, Electronic effect induced by variation of size for Pd clusters in 1,3-butadiene hydrogenation, Z. Phys. D 12 (1989) 587.

[91] C. Kuhrt, M. Harsdorff, Photoemission and electron microscopy of small supported palladium clusters, Surf. Sci. 245 (1991) 173.

[92] A. Sandell, J. Libuda, P.A. Brühwiler, S. Andersson, A.J. Maxwell, M. Bäumer, N. Mårtensson, H.-J. Freund, Interaction of CO with Pd clusters supported on a thin alumina film, J. Vac. Sci. Technol. A 14 (1996) 1546.

[93] M. DeCrescenzi, M. Diociaiuti, L. Lozzi, P. Picozzi, S. Santucci, Surface electron-energy-loss fine-structure investigation on the local structure of copper clusters on graphite, Phys. Rev. B 35 (1987) 5997.

[94] D.R. Rainer, D.W. Goodman, in: R.M. Lambert, G. Pacchioni (Eds.), Chemisorption and Reactivity on Supported Clusters and Thin Films Series E, vol. 331, Kluwer, Dordrecht, 1997, p. 27.

[95] M. Valden, X. Lai, D.W. Goodman, Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties, Science 281 (1998) 1647.

[96] U. Kreibig, M. Vollmer (Eds.), Optical Properties of Metal Clusters, Springer Series in Materials Science, vol. 25, Springer, Berlin, 1995.

[97] F. Stietz, F. Träger, Surface plasmons in nanoclusters: elementary electronic excitations and their applications, Phil. Mag. B 79 (1999) 1281.

[98] K.-P. Charlé, L. König, S. Nepijko, I. Rabin, W. Schulze, The surface plasmon resonance of free and embedded Ag-Clusters in the size range $1,5\ \mathrm{nm} < D < 30\ \mathrm{nm}$, Crystal Res. Technol. 33 (1998) 1085.

[99] N. Nilius, N. Ernst, H.-J. Freund, Photon emission spectroscopy of individual oxide-supported silver clusters in the STM, Phys. Rev. Lett. 84 (2000) 3994.

[100] J.K. Gimzewski, B. Reihl, J.K. Sass, R.R. Schlittler, Photon emission experiment with the scanning tunneling microscope, J. Microsc. 152 (1988) 325.

[101] J. Evans, B. Hayden, F. Mosselman, A. Murray, Adsorbate induced phase changes of rhodium on $TiO_2(110)$, Surf. Sci. 279 (1992) L159.

[102] J. Evans, B. Hayden, F. Mosselman, A. Murray, The chemistry of rhodium on $TiO_2(110)$ deposited by MOCVD of $[Rh(CO)_2Cl]_2$ and MVD, Surf. Sci. 301 (1994) 61.

[103] M. Frank, R. Kühnemuth, M. Bäumer, H.-J. Freund, Vibrational spectroscopy of CO adsorbed on supported ultra-small transition metal particles and single metal atoms, Surf. Sci. 454–456 (2000) 968.

[104] M. Frank, R. Kühnemuth, M. Bäumer, H.-J. Freund, Oxide-supported Rh particle structure probed with carbon monoxide, Surf. Sci. 427/428 (1999) 288.

[105] P. Uvdal, P.-A. Karlsson, C. Nyberg, S. Andersson, N.V. Richardson, On the structure of dense CO overlayers, Surf. Sci. 202 (1988) 167.

[106] T. Giessel, O. Schaff, C.J. Hirschmugl, V. Fernandez, K.M. Schindler, A. Theobald, S. Bao, R. Lindsay, W. Berndt, A.M. Bradshaw, C. Baddeley, A.F. Lee, R.M. Lambert, D.P. Woodruff, A photoelectron diffraction study of ordered structures in the chemisorption system Pd(111)-CO, Surf. Sci. 406 (1998) 90.

[107] G. Kisters, J.G. Chen, S. Lehwald, H. Ibach, Adsorption of CO on the unreconstructed and reconstructed Ir(100) surface, Surf. Sci. 245 (1991) 65.

[108] J. Lauterbach, R.W. Boyle, M. Schick, W.J. Mitchell, B. Meng, W.H. Weinberg, The adsorption of CO on Ir(111) investigated with FT-IRAS, Surf. Sci. 350 (1996) 32.

[109] F. Solymosi, È. Novàk, A. Molnàr, Infrared spectroscopic study on CO-induced structural changes of iridium on an alumina support, Phys. Chem. 94 (1990) 7250.

[110] T.W. Voskobojnikov, E.S. Shpiro, H. Landmesser, N.I. Jaeger, G. Schulz-Ekloff, Redox and carbonylation chemistry of iridium species in the channels of H-ZSM-5 zeolite, J. Mol. Catal. A-Chem. 104 (1996) 299.

[111] K. Wolter, O. Seiferth, H. Kuhlenbeck, M. Bäumer, H.-J. Freund, Infrared spectroscopic investigation of CO adsorbed on Pd aggregates deposited on an alumina model support, Surf. Sci. 399 (1998) 190.

[112] C. DeLaCruz, N. Sheppard, In situ IR spectroscopic study of the adsorption and dehydrogenation of ethene on a platinum-on-silica catalyst between 100 and 294 K, J. Chem. Soc. Faraday Trans. 93 (1997) 3569.

[113] G.A. Beitel, A. Laskov, H. Oosterbeek, E.W. Kuipers, Polarization modulation infrared reflection absorption spectroscopy of CO adsorption on Co(0001) under a high-pressure regime, J. Phys. Chem. 100 (1996) 12494.

[114] G.A. Somorjai, G. Rupprechter, Molecular studies of catalytic reactions on crystal surfaces at high pressures and high temperatures by infrared-visible sum frequency generation (SFG) surface vibrational spectroscopy, J. Phys. Chem. B 103 (1999) 1623.

[115] H. Härle, A. Lehnert, U. Metka, H.R. Volpp, L. Willms, J. Wolfrum, In situ detection and surface coverage measurements of CO during CO oxidation on polycrystalline platinum using sum frequency generation, Appl. Phys. B 68 (1999) 567.

[116] T. Dellwig, G. Rupprechter, H. Unterhalt, H.-J. Freund, Bridging the pressure and materials gaps: High pressure sum frequency generation study on supported Pd nanoparticles, Phys. Rev. Lett. 85 (2000) 776.

[117] U. Heiz, W.-D. Schneider, in: K.H. Meiwes-Broer (Ed.), Cluster Surface Interaction, Springer, Berlin, 1999.

[118] F. Vanolli, U. Heiz, W.-D. Schneider, Vibrational coupling of CO adsorbed on monodispersed Ni_{11} clusters supported on magnesia, Chem. Phys. Lett. 277 (1997) 527.
[119] U. Heiz, A. Sanchez, S. Abbet, W.-D. Schneider, Catalytic oxidation of carbon monoxide on monodispersed platinum clusters: each atom counts, J. Am. Chem. Soc. 121 (1999) 3214.
[120] U. Heiz, W.-D. Schneider, Nanoassembled model catalysts, J. Phys. D: Appl. Phys. 33 (2000) 85.
[121] U. Heiz, A. Sanchez, S. Abbet, W.D. Schneider, The reactivity of gold and platinum metals in their cluster phase, Eur. Phys. J. D 9 (1999) 35.
[122] Y. Iwasawa (Ed.), X-ray Absorption Fine Structure for Catalysts and Surfaces, Series on Synchrotron Radiation Techniques and Applications, vol. 2, World Scientific, Singapore, 1996.
[123] L. Reimer, Transmission Electron Microscopy: Physics of Image Formation and Microanalysis, Springer, Berlin, 1997.
[124] Seventh Annual Workshop–European Synchrotron Light Sources, BESSY, Berlin, 1999.
[125] Das Jahrbuch des Forschungszentrums, DESY, Hamburg, 2000.
[126] Y.R. Shen, The Principles of Nonlinear Optics, Wiley, New York, 1984.
[127] J. Stöhr, NEXAFS spectroscopy, Springer Series in Surface Sciences, vol. 25, Springer, Berlin, 1992.
[128] W. Kuch, R. Fromter, J. Gilles, D. Hartmann, C. Ziethen, C.M. Schneider, G. Schonhense, W. Swiech, J. Kirschner, Element-selective magnetic imaging in exchange-coupled systems by magnetic photoemission microscopy, Surf. Rev. Lett. 5 (1998) 1241.
[129] J. Falta, D. Bahr, G. Materlik, B.H. Muller, M. Horn-Von-Hoegen, X-ray characterization of buried delta layers, Surf. Rev. Lett. 5 (1998) 145.
[130] DESY Forschungs- und Entwicklungsprogramm, DESY, Hamburg, 1999–2000.
[131] R. Wichtendahl, R. Fink, H. Kuhlenbeck, D. Preikszas, H. Rose, R. Spehr, P. Hartel, W. Engel, R. Schlögl, H.-J. Freund, A.M. Bradshaw, G. Lilienkamp, T. Schmidt, E. Bauer, G. Benner, E. Umbach, SMART: an aberration-corrected XPEEM/LEEM with energy filter, Surf. Rev. Lett. 5 (1998) 1249.
[132] H. Ade, W. Yang, S.L. English, J. Hartman, R.F. Davis, R.J. Nemanich, V.N. Litvinenko, L.V. Pinayev, Y. Wu, J.M.J. Madey, A free electron laser—photoemission electron microscope system (FEL-PEEM), Surf. Rev. Lett. 5 (1998) 1257.
[133] T. Duden, E. Bauer, Spin-polarized low energy electron microscopy, Surf. Rev. Lett. 5 (1998) 1213.
[134] T.R. Linderoth, S. Horch, E. Laegsgaard, I. Stensgaard, F. Besenbacher, Dynamics of Pt adatoms and dimers on Pt(1 1 0)-(1 × 2) observed directly by STM, Surf. Sci. 402–404 (1998) 308.
[135] B.C. Stipe, M.A. Rezaei, W. Ho, Single-molecule vibrational spectroscopy and microscopy, Science 280 (1998) 1732.
[136] F.M. Hoffmann, G.P. Williams, Synchrotron radiation in the far infrared: infrared reflection absorption spectroscopy, in: W. Eberhardt (Ed.), Applications of Synchrotron Radiation—High Resolution Studies of Molecules and Molecular Adsorbates on Surfaces, Springer Series in Surface Sciences, vol. 35, Springer, Berlin, 1995, p. 263.
[137] A. Campion, Raman spectroscopy in vibrational spectroscopy of molecules on surfaces, in: J.T. Yates, T.E. Madey (Eds.), Methods of Surface Characterization, vol. 1, Plenum, New York, 1987, p. 345.
[138] Y.T. Chua, P.C. Stairs, A novel fluidized bed technique for measuring UV Raman spectra of catalysts and adsorbates, J. Catal. 196 (2000) 66.
[139] K. Watanabe, Y. Matsumoto, M. Kampling, K. Al-Shamery, H.-J. Freund, Photochemistry of methane on Pd/Al_2O_3 model catalyst: control of photochemistry on transition metal surfaces, Angew. Chem. Int. Ed. 38 (1999) 2192.
[140] C. Becker, C.R. Henry, Cluster size dependent kinetics for the oxidation of CO on a Pd/MgO(1 0 0) model catalyst, Surf. Sci. 352 (1996) 457.
[141] I. Meusel, J. Hoffmann, J. Hartmann, M. Heemeier, M. Bäumer, J. Libuda, H.-J. Freund, The interaction of oxygen with alumina-supported palladium particles, Catal. Lett. 71 (2001) 5.
[142] V.P. Zhdanov, B. Kasemo, Simulations of the reaction kinetics on nanometer supported particles, Surf. Sci. Rep. 39 (2000) 25.
[143] H. Eyring, J. Phys. Chem. 3 (1935) 107.
[144] M.G. Evans, M. Polanyi, Trans. Faraday Soc. 31 (1935) 875.
[145] M.G. Evans, M. Polanyi, Trans. Faraday Soc. 33 (1937) 448.
[146] A.H. Zewail (Ed.), Femtochemistry—Ultrafast Dynamics of the Chemical Bond, vols. 1 and 2, World Scientific Publishing, Singapore, 1994.
[147] H. Petek, S. Ogawa, Femtosecond time-resolved two-photon photoemission studies of electron dynamics in metals, Progr. Surf. Sci. 56 (1998) 239.
[148] M.J. Feldstein, P. Vöhringer, W. Wang, N.F. Scherer, Femtosecond optical spectroscopy and scanning probe microscopy, J. Phys. Chem. 100 (1996) 4739.
[149] T. Klar, M. Perner, S. Grosse, G. von Plessen, W. Spirkl, J. Feldmann, Surface-plasmon resonances in single metallic nanoparticles, Phys. Rev. Lett. 80 (1998) 4249.