



Critical Review

Synthesis and catalytic properties of metal nanoparticles: Size, shape, support, composition, and oxidation state effects

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ARTICLE INFO

Available online 22 January 2010

Keywords:

Catalysis
Nanoparticle
Cluster
Reactivity
XPS
EXAFS
TPD
STM
Mass spectrometry
Electrochemistry

ABSTRACT

Exciting new opportunities are emerging in the field of catalysis based on nanotechnology approaches. A new understanding and mastery of catalysis could have broad societal impacts, since about 80% of the processes in the chemical industry depend on catalysts to work efficiently. Efforts in surface science have led to the discovery of new heterogeneous catalysts, however, until recently the only way to develop new or improved catalysts was by empirical testing in trial-and-error experiments. This time-consuming and costly procedure is now rapidly being replaced by rational design methods that utilize fundamental knowledge of catalysts at the nanoscale. The advent of nanoscience and nanotechnology is providing the ability to create controlled structures and geometries to investigate and optimize a broad range of catalytic processes. As a result, researchers are obtaining fundamental insight into key features that influence the activity, selectivity, and lifetime of nanocatalysts. This review article examines several new findings as well as current challenges in the field of nanoparticle based catalysis, including the role played by the particle structure and morphology (size and shape), its chemical composition and oxidation state, and the effect of the cluster support.

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1. Introduction to nanocatalysis

Heterogeneous catalysis has received a tremendous amount of interest, both from a scientific and an industrial perspective. This is demonstrated by the 2007 Nobel Prize in Chemistry awarded to Prof. Ertl, a pioneer in introducing surface science techniques to the field of heterogeneous catalysis leading to a deeper understanding of how chemical reactions take place at surfaces [1–8]. Heterogeneous catalysis has an enormous impact on the world economy, since more than 90% of chemical manufacturing processes utilize catalysts [9]. Catalysts are also essential in converting hazardous waste into less harmful products as, for example, in the automobile exhaust system. The efficient, controlled, and

cost-effective design of catalysts is thus a goal of great importance; one that promises to supersede present trial and error approaches. Catalysis is also one of the scientific disciplines in which even small advances, when based on fundamental research, can have a very significant impact on society. Due to the enormous scale of commercial applications, progress in catalysis can have a positive economic as well as environmental impact. More specifically, the automotive and power generation industries are the sectors that stand to benefit most directly from breakthroughs that are expected to occur in the field of catalysis.

One area of catalysis that is developing at a rapid pace is nanocatalysis. Striking novel catalytic properties including greatly enhanced reactivities and selectivities have been reported for nanoparticle (NP) catalysts as compared to their bulk counterparts. In order to harness the power of these nanocatalysts, a detailed

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understanding of the origin of their enhanced performance is needed. Many experimental studies on nanocatalysts have focused on correlating catalytic activity with particle size. While particle size is an important consideration, many other factors such as geometry, composition, oxidation state, and chemical/physical environment can play a role in determining NP reactivity. However, the exact relationship between these parameters and NP catalytic performance may be system dependent, and is yet to be laid out for many nanoscale catalysts. Clearly, a systematic understanding of the factors that control catalyst reactivity and selectivity is essential if trial and error methods are to be avoided.

One of the most interesting model systems for researchers in the field of catalysis is gold NPs. Although bulk gold samples are practically inert, nanometer-sized gold particles have been proven to be highly active for several reactions, including low-temperature oxidation of CO, partial oxidation of hydrocarbons, the water–gas shift reaction [10–12], and reduction of nitrogen oxides when dispersed over certain oxides [13,14] and carbides [15,16]. Despite the large amount of work on this topic, the mechanism of Au NP reactivity has remained elusive [17–22], with the role of the oxide substrate being the main subject of debate. Examples of related discussions in the current literature follow. Lopez et al. [17] have argued that undercoordinated Au atoms in NPs play the main role in the reactivity, while the substrate is of little significance. The authors claim that charge transfer from oxygen vacancies in the support to the Au NPs as well as the interaction of adsorbates with the nanoparticle–support interface do not significantly contribute to the observed activity. Further, Chen and Goodman [18] report that an enhancement in reactivity is not limited to Au NPs, but that a bilayer of Au on TiO₂(110) is just as effective for CO oxidation. Campbell [19], however, argues that the Au bilayer might not completely wet the oxide surface and that the oxide/metal interface may in fact be of significance. A recent article by Goodman's group [23] also highlighted that ultrathin (bilayer) gold films deposited on reduced TiO₂ display activities similar to those of gold NPs. Therefore, although other factors such as nanoparticle–support interactions may also play a role in the enhanced reactivity of metal clusters, according to this group it is the NP's height and not its diameter that is the critical structural parameter affecting its catalytic properties. Fig. 1 displays a comparison of the CO₂ formation rate obtained from different Au structures, with the highest reactivity being observed for a

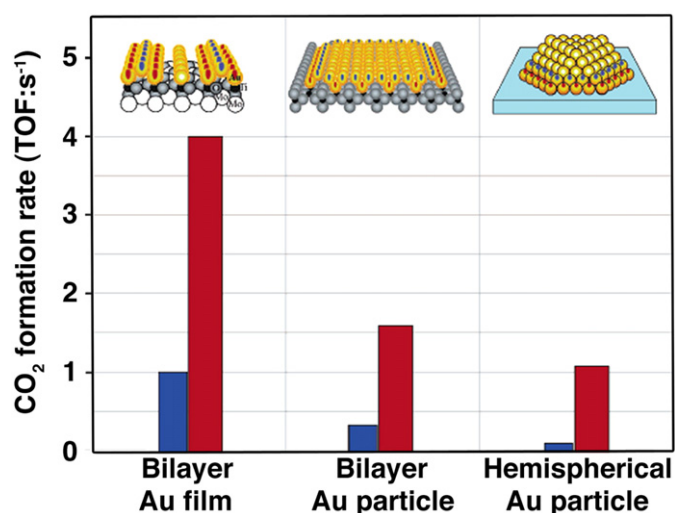


Fig. 1. Comparison of catalytic activities (turnover frequency, TOF, in s⁻¹) for CO oxidation on a bilayer Au film [Mo(112)-1 × 3-(Au, TiO_x)], a bilayer Au NP [Au/TiO₂(110)], and an hemispherical Au NP supported on high-surface area TiO₂ with a mean particle size of ~3 nm. The inserts show structural models using red and blue marks to indicate active sites.

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bilayer gold film [23]. While supported Au clusters provide the most dramatic example of nanocatalytic phenomena, palladium, platinum, and several other metal NPs on oxide supports also exhibit high catalytic activity. There are indications that in addition to the reduced particle size [24], metal/oxide interactions are partially responsible for the high activity [25–30].

The sections below will provide information on factors that are presently believed to play a significant role in the catalytic reactivity of supported metal clusters, with emphasis on understanding the relationship between the structure (size and shape), chemical composition, oxidation state, interparticle interactions, and reactivity of nanocatalysts. However, it should be stressed that although these elements are discussed in separate sections, this does not mean that they are independent contributing factors in nanocatalysis. To the contrary, many of these parameters are interrelated. For example, the NP support will affect the NP shape, and in many occasions it will be difficult to separate the specific role played by each of these parameters in the reactivity of supported NPs. Since the amount of published relevant material in this topical area is overwhelming, this review is by no means exhaustive. For additional reading, the excellent review articles in Refs. [23,31–45] are recommended.

2. Synthesis of active nanocatalysts

In recent years, a number of approaches have been used for the synthesis of nanoparticle catalysts including thermal evaporation in vacuum [18,46–48], electron-beam lithography and pulsed laser deposition [49–51], buffer-layer assisted growth [52–54], chemical vapor deposition [55–57], gas condensation, ionized cluster beam deposition [58,59], electrochemical deposition methods [60–64], sol–gel or colloidal techniques [65,66], deposition–precipitation and impregnation methods [67–69], molecular cluster precursors [70], etc. Some examples of the resulting structures are shown in Fig. 2.

Special emphasis has been given to the achievement of a high degree of control over the cluster size, shape, and dispersion on the support by means of reproducible, low cost, synthetic approaches (ex-situ) that are suitable to be scaled up to large substrate areas and material quantities. One of the main pre-requisites of these new approaches is the production of robust materials that preserve their initial morphologies, or at least their narrow size distribution under reaction conditions (e.g. exposure to reactants and temperature treatments), with minimum coarsening. These challenging goals are being addressed by using organic ligands for the confinement of inorganic catalysts in dendrimeric [71–73] or micellar nanoreactors [15,74–76] with predefined sizes and shapes.

However, although very promising preliminary data already exist on the success of these methods to produce reliable size-selected active catalysts, further work is still needed; in particular, that related to the development of non-aggressive approaches for the complete removal of undesired encapsulating ligands. An example is the possibility of having a residual carbon coating or metal carbide shell on the surface of NPs synthesized by means of diblock-copolymer encapsulation if the sample pre-treatment is not adequate, Fig. 3(a), (b) [76]. Such drawbacks emphasize the importance of thorough sample characterization before reactivity experiments are attempted in order to make sure that the results obtained correspond to not just morphologically well-defined, but also chemically known nanoscale systems free from poisoning synthesis-residues, Fig. 3(c), (d).

In addition, attention should be paid to how the prepared NPs and sample pre-treatment affect the morphology, structure, and electronic properties of the NP support. In some cases, the catalytic reactivity of these heterogeneous systems appears to be strongly dependent on special sites at the support itself (e.g. O-vacancies) or at the NP/support interface. Fig. 3(e),(f) illustrates the formation of TiO₂ nanostructures on TiO₂(110) surfaces coated by micellar Pt NPs during sample annealing in vacuum at elevated temperatures (>1000 °C).

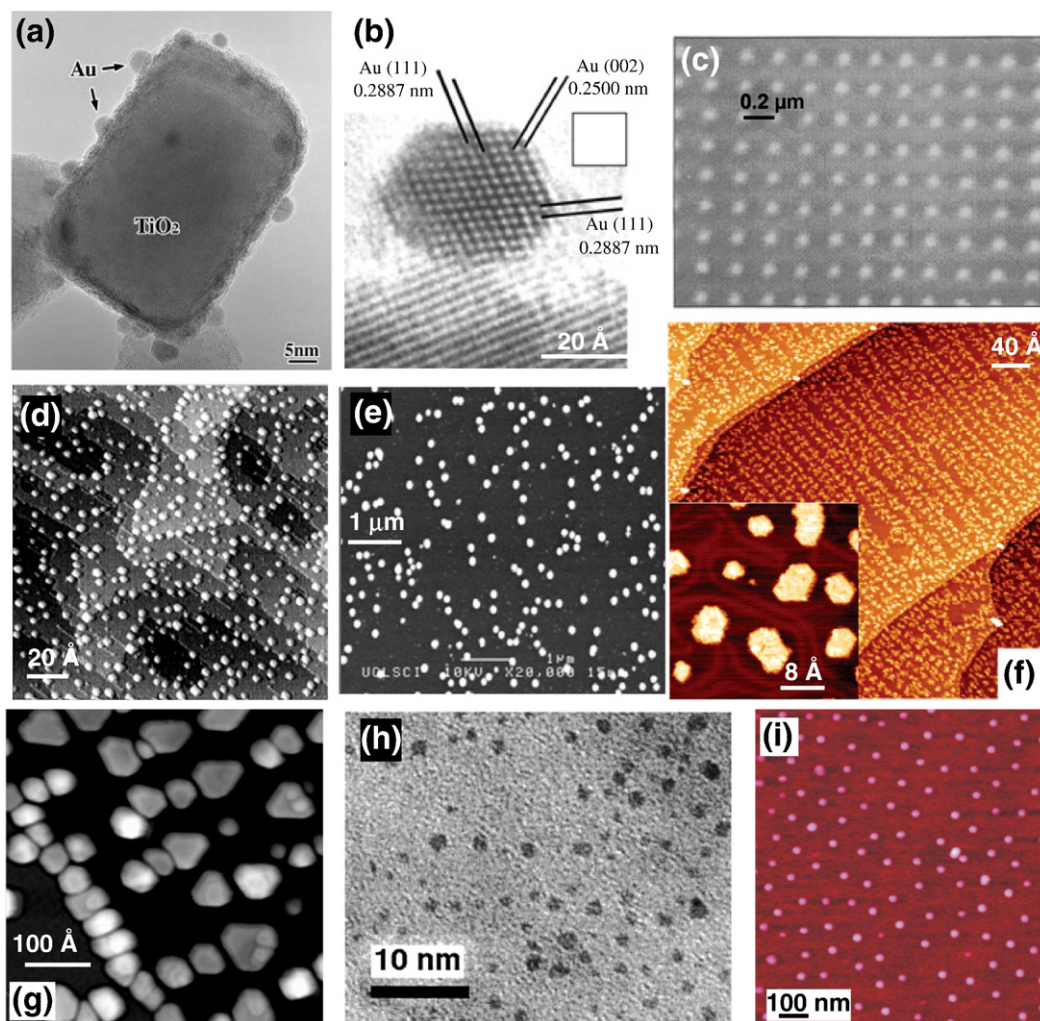


Fig. 2. (a) TEM image of Au NPs supported on nanocrystalline anatase TiO₂ prepared by the deposition–precipitation method. (b) High resolution TEM image of an ~5 nm cuboctahedral gold NP on ZnO. (c) SEM image of an array of Pt NPs fabricated by electron beam lithography. (d) STM image of Au NPs synthesized by evaporation of 1 ML of Au on TiO₂(110). (e) SEM image of Au NPs prepared by aerosol assisted chemical vapor deposition. (f) STM image of TiO₂ NPs supported on Au(111) prepared by reactive-layer-assisted deposition. (g) STM image of truncated cuboctahedron Pd NPs nucleated at steps and domain boundaries on Al₂O₃/NiAl(110). (h) TEM image of Pd NPs prepared by encapsulation in dendrimers. (i) AFM image of Ir NPs supported on SiO₂/Si(001) synthesized by encapsulation in polystyrene-vinylpyridine (PS-P2VP) micelles. Panel (a) was reprinted from Catal. Today, 36, 153, Copyright 1997, with permission from Elsevier. Panel (b) was reprinted from G.J. Hutchings, Gold Bull. 37 (2004) 3, with permission from World Gold Council. Panel (c) was reprinted with permission from A.S. Eppler et al., J. Phys. Chem. B 101 (1997) 9973. Copyright 1997, American Chemical Society. Panel (d) was reprinted from J. Molec. Catal. A, 162, X.F. Lai and D.W. Goodman, 33, Copyright 2000, with permission from Elsevier. Panel (e) was reprinted from R.G. Palgrave and I.P. Parkin, Gold Bull. 41 (2008) 66, with permission from World Gold Council. Panel (f) was reprinted with permission from Z. Song et al., Nano Lett. 5 (2005) 1327. Copyright 2005, American Chemical Society. Panel (g) was reprinted with kind permission from Springer Science + Business Media: Top. Catal. 48 (2008) 137, H.J. Freund. Panel (h) was reprinted with permission from R.M. Crooks et al., Acc. Chem. Res. 34 (2001) 181. Copyright 2001, American Chemical Society. Panel (i) was from B. Roldan Cuenya, unpublished.

3. Size effects

Since the experimental observations by Haruta et al. [67,77] of the dramatic enhancement of the catalytic activity and selectivity of highly-dispersed gold particles (<5 nm) supported on reducible metal oxides, considerable efforts have been dedicated to the investigation of the influence of NP size [67,78–83] and NP–support interaction [67,83] on the catalytic activity.

One of the most broadly studied catalytic reactions is the low-temperature oxidation of CO. Having as a common goal the understanding of catalysis at the atomic level, different models were proposed to explain the high activity of small metallic NPs [17,78,84–86]. A clear picture compiling some of the models being considered was given by Cho, Fig. 4. This cartoon includes models assigning the enhanced and size-dependent reactivity of gold clusters to different contributions, namely to: (i) small metal clusters displaying non-metallic behavior (quantum size effects), (ii) the presence of higher densities of low

coordinated atoms, (iii) excess electronic charge, and (iv) NP–support interactions (active perimeter sites). In this section, we will focus on the size-dependent aspects (i–iii) and will dedicate future sections to the importance of the cluster support (iv).

Goodman's group was the first to suggest that the high activity of small gold particles is related to quantum-size effects generated by electrons confined within a small volume [79,87]. Based on scanning tunneling spectroscopy (STS) studies, a size-dependent metal-to-semiconductor transition was observed for Au NPs deposited on TiO₂, and a correlation between the appearance of a bandgap and catalytic activity established. However, recent density functional theory (DFT) calculations by Mills et al. [88] showed that the presence of a bandgap might not be essential to the chemical activity of a cluster. Naitabdi and Cuenya [89] also reported non-metallic behavior for Au NPs smaller than ~2 nm (height) deposited on TiC [89], Fig. 5. However, although the bandgap was found to initially increase with decreasing cluster size, cluster heights below ~1.3 nm showed a decrease in the observed

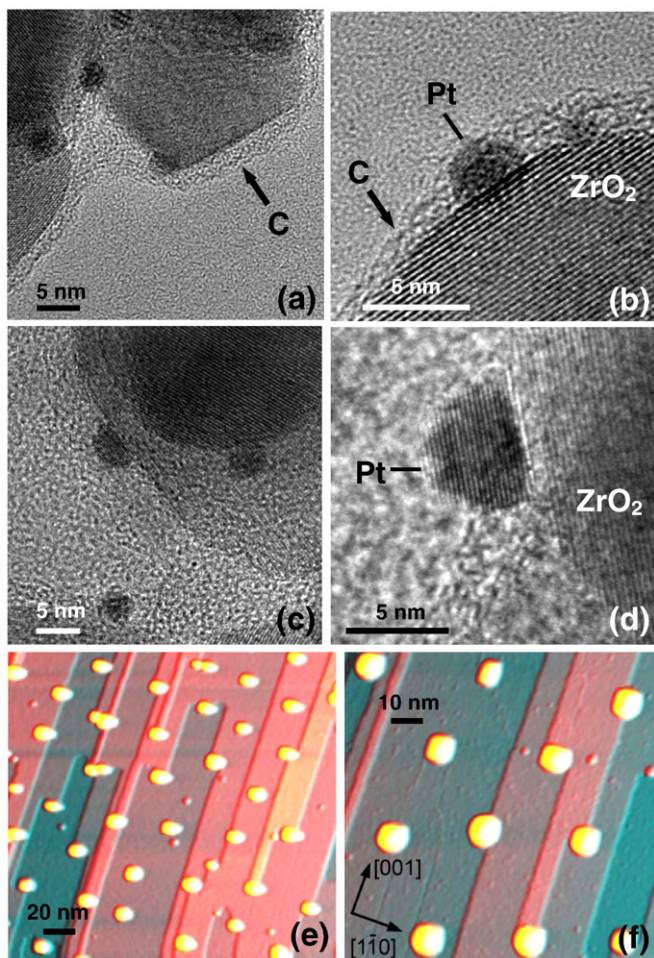


Fig. 3. TEM images of Pt NPs synthesized by encapsulation in PS-P2VP diblock copolymer micelles and supported on nanocrystalline ZrO_2 . Images (a) and (b) were taken after sample pre-treatment in H_2 at $500^\circ C$ for 8 h, while (c) and (d) correspond to analogously prepared samples annealed in O_2 . The presence of a residual polymeric layer (see arrows) was observed only on the H_2 -annealed samples (a) and (b). (e and f) STM images of micellar Pt NPs deposited on $TiO_2(110)$ taken after polymer removal by an in-situ O_2 -plasma treatment and subsequent annealing at $1040^\circ C$. The latter NPs preserve their original hexagonal substrate arrangement up to $1060^\circ C$. In addition, their presence on the TiO_2 substrate and strong NP/support interactions lead to the formation of TiO_2 nanostructures at elevated temperatures ($> 1000^\circ C$). Panels (a) and (b) were reprinted with kind permission from Springer Science + Business Media: Catal. Lett. 131 (2009) 21, J.R. Croy et al. Adapted from Naitabdi et al. [117].

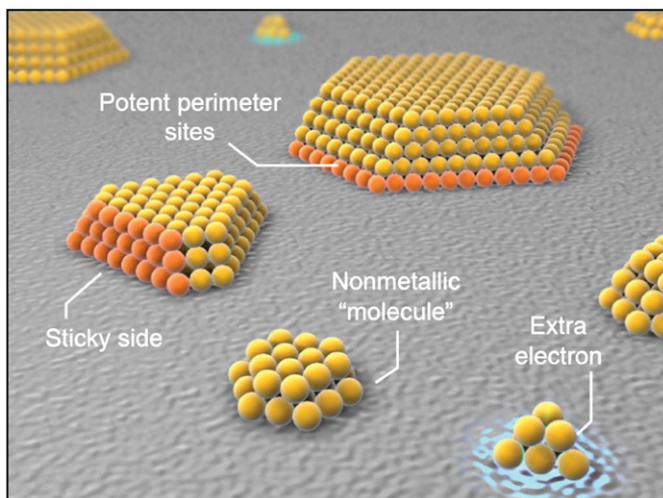


Fig. 4. Possible mechanisms responsible for the enhanced reactivity of nanoscale gold. From A. Cho, Science 299 (2003) 1684. Reprinted with permission from AAAS.

bandgap. This effect was attributed to the contribution of states from the semi-metallic TiC substrate. Thus, the unusual electronic properties of small gold NPs were assigned to a combination of quantum size effects and NP-support interactions; however, no direct correlation between modified electronic structure and chemical reactivity was established.

Increasingly positive binding energy shifts with decreasing particle size have been measured for small metallic clusters by X-ray photoelectron spectroscopy (XPS) [e.g. Fig. 6]. The origin of such shifts is debated; they have been commonly assigned to changes in the electronic structure of the clusters (initial state effects) [90,91], as well as to positive charge left on the cluster surface during the photoemission process (final state effects) [75,92]. This effect is illustrated in Fig. 6 by Ono et al. [15], where $Au^{0-4f_{7/2}}$ binding energies measured on Au NPs supported on TiC have been displayed as a function of the cluster height. The largest shift, $+0.8$ eV, was observed for the smallest NPs investigated (~ 1.9 nm), while a binding energy close to

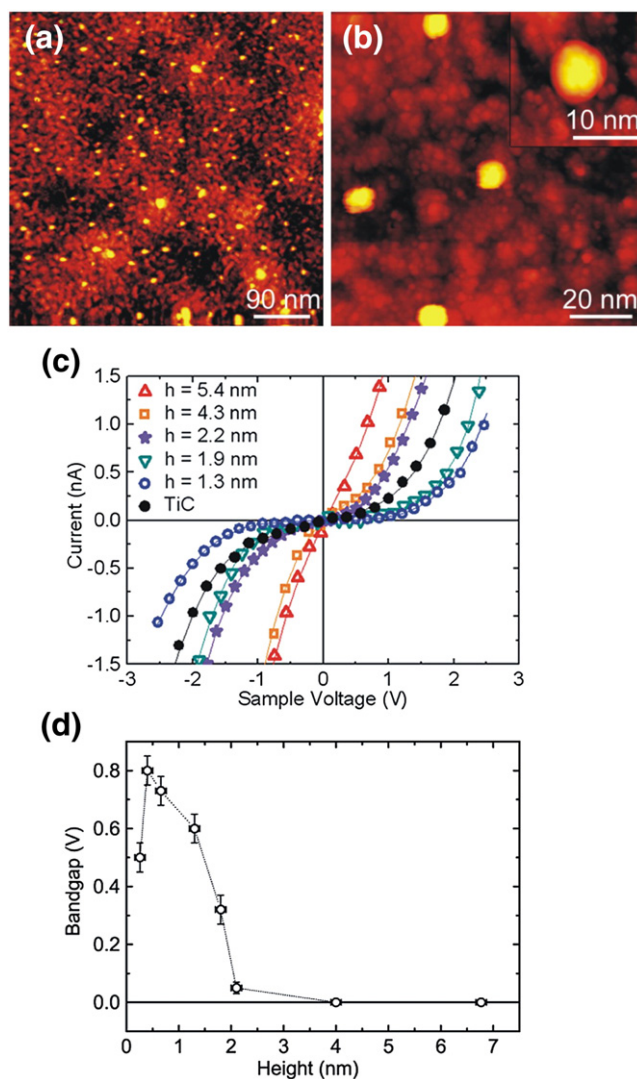


Fig. 5. STM images obtained on size-selected Au NPs prepared by micelle encapsulation and self-assembled on an ultrathin polycrystalline TiC film. The scanned area was (a) $500\text{ nm} \times 500\text{ nm}$, and (b) $100\text{ nm} \times 100\text{ nm}$. The inset in (b) (top corner) shows one of the NPs where current-voltage (I - V) curves were measured. (c) STS I - V curves obtained in the center of Au NPs of different heights (h) supported on titanium carbide (TiC). The I - V curves were acquired at room temperature. Only a selected data set and the corresponding fit have been plotted for clarity. (d) Bandgap versus NP height obtained from normalized differential conductivity curves $(dI/dV)/(I/V)$ based on the STS data shown in (c). Reprinted with permission from A. Naitabdi et al., Appl. Phys. Lett. 89 (2006) 043101. Copyright 2006, American Institute of Physics.

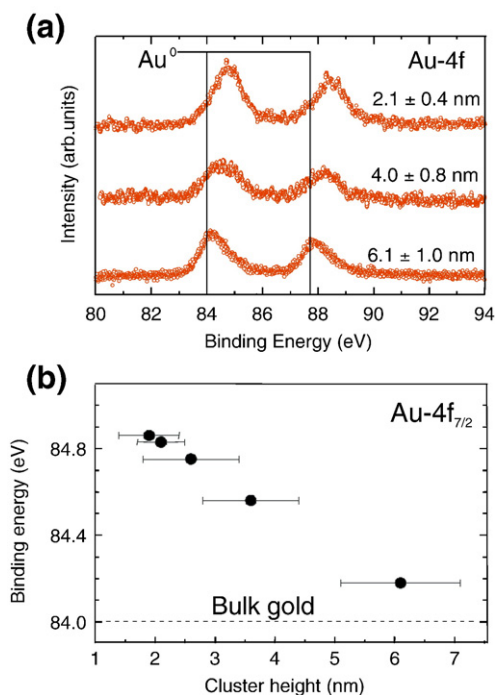


Fig. 6. (a) XPS spectra (Al K α = 1486.6 eV) corresponding to the Au-4f core level of Au NPs supported on polycrystalline TiC. The corresponding NP heights are indicated in the graph. (b) Binding energy versus cluster height obtained from the XPS Au⁰-4f_{7/2} spectra shown in (a). Different cluster sizes were obtained by using encapsulating PS-P2VP polymers with distinct molecular weights and by modifying the relative gold/polymer concentration. Reprinted from Surf. Sci., 600, L.K. Ono et al., 5041, Copyright 2006, with permission from Elsevier.

bulk gold was measured for ~6 nm large clusters. In addition, the structure of the cluster support might also play a role on the BE shifts observed on small metal clusters. DFT calculations by Yang and Wu [93] suggested that the positive core-level shifts measured on Au NPs supported on MgO(001) and TiO₂(110) could be related to the presence of oxygen vacancies in the supports.

It has long been accepted that the roughness of surfaces plays a vital role in catalysis [94–96]. For example, enhanced chemical activity has been observed for stepped Au(211) [84] and Au(332) [97] surfaces as compared to smooth Au(111) surfaces. DFT Calculations by Mills et al. [88] also demonstrated that the roughness of the surface, i.e., the presence of highly undercoordinated atoms, is important for the dissociation of O₂. A size-dependency in the electro-catalytic oxidation of CO over size-selected Au NPs deposited on indium tin oxide (ITO) was observed by Roldan et al. [75], with the smallest NPs (~1.5 nm) providing the highest normalized current densities, Fig. 7. Temperature programmed desorption (TPD) studies of CO adsorption on several submonolayer Au coverages, deposited on Al₂O₃, FeO(111), and Fe₃O₄(111) [83,98] indicated that irrespective of the support considered, the smaller Au NPs adsorbed CO more strongly (higher TPD desorption temperatures) than larger clusters, Fig. 8. CO₂ TPD experiments by Ono et al. [15] on low-temperature CO oxidation over size-selected gold NPs supported on TiC [Fig. 9] revealed an enhancement of the catalytic activity with decreasing particle size. In addition, a shift towards lower CO₂ desorption temperatures was observed with decreasing cluster size. All samples showed two desorption features that were assigned to steps/kinks in the gold surface (γ -state) and to the Au–TiC interface (π -state), Fig. 9(b). Based on DFT calculations on gold surfaces, Mavrikakis et al. [84] found that CO, O, and O₂ preferentially chemisorb on stepped surfaces. The authors concluded that the enhanced reactivity of small particles could be related to their high step densities as well as to size-dependent surface strain [84,99]. This is in agreement with previous experimental observations by Yates et al. [100,101]. Atomic beam surface scattering experiments combined with adsorption calorimetry measurements by

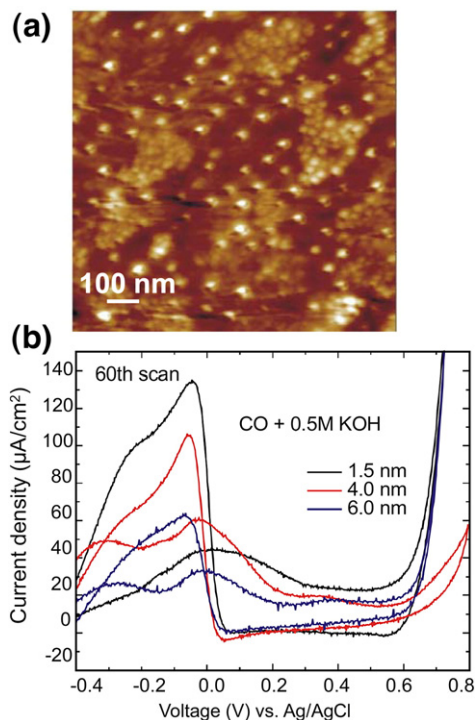


Fig. 7. (a) AFM image of Au NPs supported on polycrystalline ITO [In₂O₃ (90%)–SnO₂ (10%) (200 nm)/Glass]. (b) Electrochemical oxidation of CO. Cyclic voltammograms measured for three different average Au NP sizes (1.5 nm, 4.0 nm, and 6 nm) dip-coated onto ITO after saturation of a 0.5 M KOH solution with CO (60th scan). Current densities normalized by the total gold surface area are displayed. The voltages indicated use as reference a Ag/AgCl electrode.

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Starr and Campbell [102,103] also revealed large differences between the activation energies for adsorption on step versus terrace sites for Pb adsorbed on Mo(100), with stronger binding on step sites, Fig. 10.

A review article by Lopez et al. [17] compiling available experimental data on CO oxidation by gold concluded that the particle size (and not the support) was the determining factor controlling the catalyst's performance. The authors pointed out that the density of low-coordinated sites affects strongly the chemical activity and proposed a $\sim 1/d^3$ scaling law for the activity, with d being the particle diameter.

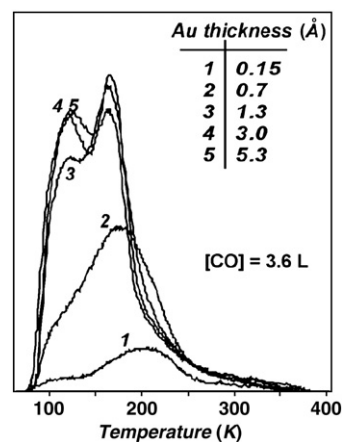


Fig. 8. CO TPD spectra for different Au coverages deposited on Al₂O₃/NiAl(110). A CO coverage of 3.6 Langmuir was used [83]. With kind permission from Springer Science + Business Media: Catal. Lett. 86 (2003) 211, S.K. Shaikhutdinov et al.

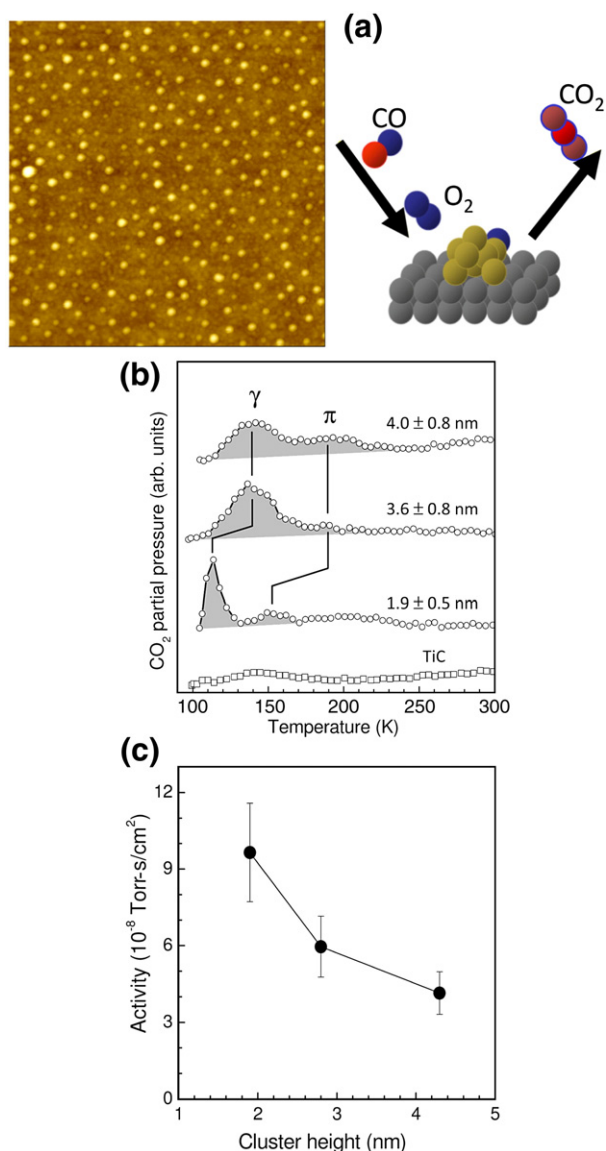


Fig. 9. (a) (left) AFM image of size-selected gold NPs synthesized by micelle encapsulation and deposited on an ultrathin polycrystalline TiC film. The image was taken after annealing in UHV at 500 °C and subsequent in-situ CO oxidation. (right) Schematic drawing of a CO oxidation reaction over supported gold clusters. (b) CO₂ TPD spectra from three Au/TiC samples with different average cluster heights (1.9 to 4 nm) but identical interparticle distances and of a gold-free TiC substrate. The samples were dosed with 0.6 L of CO and 0.3 L of O₂ at ~95 K, and a linear heating ramp of $\beta = 5$ K/s was used. The area under the peak is highlighted indicating the integration region taken in the quantitative activity analysis. (c) Normalized CO oxidation activity of Au NPs displayed as a function of the average NP height. The total gold surface area has been used in the normalization. The NP shape was determined by using a half-ellipsoid model (pancake-like particle) with average heights and diameters obtained by STM. Reprinted from "L. K. Ono et al., Surf. Sci." 600, 5041. Copyright 2006, with permission from Elsevier.

Another factor that is believed responsible for the enhanced reactivity of small clusters is their ability to transform between different energetically favorable isomers in the course of a chemical reaction [104,105].

In summary, it should be evident from the description above that the underlying origin of the distinct changes observed in the catalytic reactivity of NPs as a function of the NP size is still an open question. In my opinion, it is not a single, unique cause which results in the enhanced catalytic activity and selectivity observed for small NPs, but rather, several of the above mentioned factors acting in parallel. For instance, with decreasing NP size, the surface to volume ratio increases, resulting in a larger number of low-coordinated atoms available for interaction

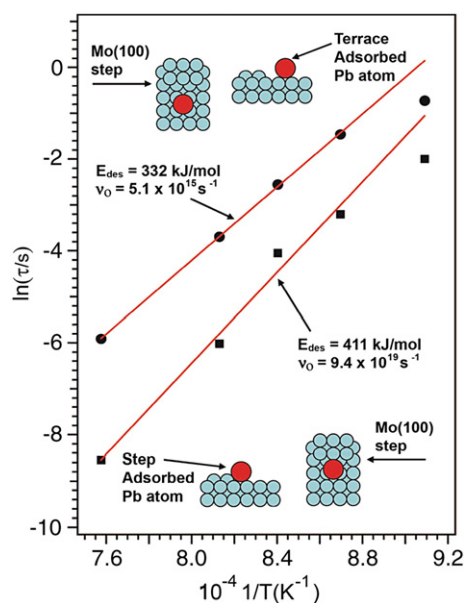


Fig. 10. Arrhenius plots obtained from the fits of desorption traces measured via mass spectrometry following pulsed deposition of Pb onto Mo(100). τ describes the residence time of Pb atoms on the Mo surface. The desorption activation barriers and pre-exponential desorption factors for Pb atoms adsorbed on step and terrace sites are indicated. Reprinted with permission from D.E. Starr and C.T. Campbell, J. Am. Chem. Soc. 130 (2008) 7321. Copyright 2008, American Chemical Society.

with chemical adsorbates. The distinct electronic properties of such sites are also expected to play a role in chemical reactivity by, for example, facilitating the dissociation of reactants or by stabilizing intermediate reaction species. Furthermore, size-effects in NP catalysis might also be understood in terms of the distinct NP/support interactions present. Such interactions can be electronic (NP/support charge transfer) or structural in nature (strain effects at the NP/support interface) or a combination of both. In addition, the particle size also plays an important role in the stability of surface oxides on clusters. This can affect the reactivity of certain NPs, since several metal oxides (e.g. RuO₂ [106]) have been proven more active than the pure metals. The effect of the oxidation state will be discussed in more detail in a subsequent section.

4. Interparticle distance effects

A key parameter that should be taken into consideration in the rational design of improved nanocatalysts is their long-term stability under reaction conditions. In-situ scanning tunneling microscopy (STM) studies conducted in Goodman's group [107–109] revealed modifications in the size and distribution of gold and silver NPs evaporated on TiO₂(110), upon room temperature (RT) exposure to CO/O₂ (2:1) and O₂ at high pressure (13.33 mbar). Because both gas dosing experiments resulted in Ostwald ripening and a comparable bimodal size distribution, the coarsening was attributed to Au–Au bond weakening induced by O₂. Freund's group [110] also identified structural transformations when Au NPs deposited on FeO(111) films were exposed to CO/O₂ and CO environments at elevated pressures (2 mbar). The authors concluded that CO exposure leads to the formation of mobile Au species by weakening the cluster–support bond.

In order to obtain further insight into the stability of nanocatalysts upon chemical adsorption, well-defined material systems with controlled and tunable size and interparticle distances are needed. Somorjai's group [111,112] studied the ethylene hydrogenation reaction over Pt NPs (28 to 50 nm in diameter) produced by electron-beam lithography and found no reaction rate changes due to NP size or arrangement on SiO₂ and Al₂O₃ substrates. Furthermore, an annealing treatment at 573 K in NO₂ (1 × 10⁻⁶ Torr) and subsequent CO exposure (1 × 10⁻⁷ Torr) did not modify the particle morphology or distribution. However, similarly

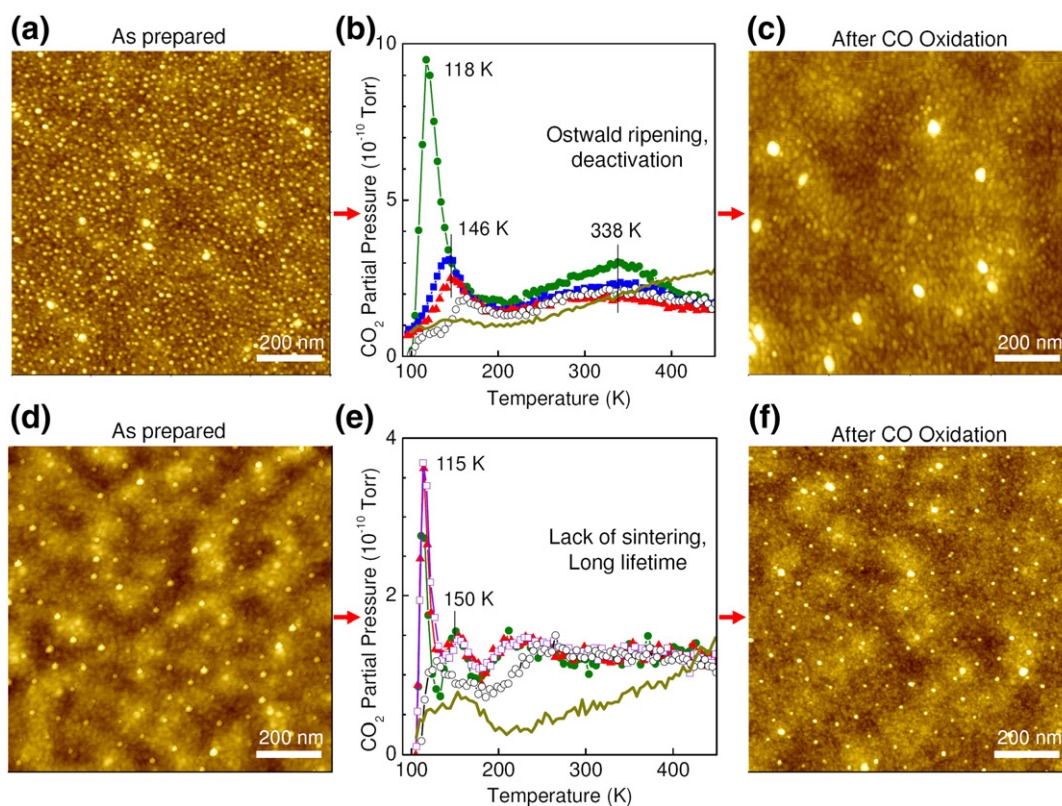


Fig. 11. AFM images of size-selected Au NPs synthesized by inverse micelle encapsulation using two different PS-PVP diblock-copolymers and deposited on polycrystalline TiC. The average NP height in both samples is ~ 2 nm and the average interparticle distances are ~ 30 nm [sample #1, (a and c)] and ~ 80 nm [sample #2, (d and f)]. The images were acquired after polymer removal by annealing at 500°C in UHV (a and d) and after subsequent CO oxidation (c and f). Sample #1 was exposed to five successive CO oxidation TPD cycles and sample #2 to seventeen cycles. The middle graphs (b and e) contain CO_2 TPD spectra of the same two samples measured in repeated cycles under the same dosing conditions CO (0.6 L) + O_2 (0.3 L) at $\sim 95\text{ K}$ and heated with a linear ramp $\beta = 5\text{ K/s}$. A blank TPD spectrum (open circles) was taken for reference without the exposure of reactive gases. Five cycles of CO oxidation were run on sample #1 and the corresponding first (solid circles), third (squares), fifth (triangles) TPD spectra are shown in (b). On sample #2 (e), seventeen cycles of CO oxidation were run and three of them are shown first (solid circles), tenth (triangles), and seventeenth (open squares). The solid lines indicate the CO_2 signal, after dosing with gases, from the corresponding gold-free TiC substrates.

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prepared but larger Pt NPs (750 nm diameter) by Johansson et al. [113], showed disintegration upon exposure at 748 K to H_2/O_2 mixtures diluted in Argon. Laurin et al. [114] also detected the formation of a ring of small NPs around large (500 nm) Pd clusters supported on SiO_2 upon exposure to O_2 ($\sim 4 \times 10^{-4}\text{ mbar}$) at 650 K and subsequent oxygen removal by CO .

Better understanding is still required regarding the role interparticle interactions may play in chemical reactivity. Recent work by Roldan's group [15,16,89,115–119] demonstrated that simple and inexpensive (as compared to clusters grown by e-beam lithography) chemical synthesis routes such as encapsulation in PS-P2VP diblock copolymers can be used to produce size-selected, hexagonally-ordered arrays of small ($0.5\text{--}30\text{ nm}$) catalytically active metal NPs. Thanks to the ordered cluster arrangement obtained using this method, cluster mobility [117] and chemically-induced coarsening processes can be easily monitored [16]. As an example, Ono et al. [16] showed that the catalytic activity and stability of gold NPs uniformly dispersed on polycrystalline TiC films exhibited a strong dependence on interparticle distance, Fig. 11. In this work, two samples with similar average NP sizes ($\sim 2\text{ nm}$), but different average interparticle distances ($\sim 30\text{ nm}$ and $\sim 80\text{ nm}$), were synthesized using diblock copolymer encapsulation, Fig. 11 (left). Their chemical reactivity was investigated by TPD [Fig. 11 (center)], and reactive coarsening and subsequent deactivation was observed for the sample with the smallest interparticle distance, Fig. 11 (right, top). The system with the largest average interparticle distance showed higher stability against agglomeration and longer lifetime, Fig. 11 (right, bottom). Interestingly, morphological changes have been observed in the NP samples with small interparticle distance upon low pressure ($\sim 10^{-8}\text{ mbar}$) gas dosing at 95 K .

The results described above emphasize the importance of taking into account not just the initial NP size, but also their distribution on the substrate surface in order to improve the lifetime of nanocatalysts, since dramatic morphological changes (temperature- and chemically-induced) can occur under realistic reactions conditions.

5. Shape effects

Among others, Haruta et al. [78] suggested that the catalytic activity of gold NPs for CO oxidation depends strongly on the NP-support contact area, i.e. on the particle's shape. Different preparation methods yield different shapes, and hemispherical particles were found by this group to perform better than spherical particles. These results also indicated that catalytic reactions may occur at the perimeter interfaces around Au particles, where the fraction of step sites increases significantly with decreasing particle size [78]. Reference [120] is an excellent review by C. R. Henry discussing a number of aspects related to the morphology of supported NPs, including the stability of different NP shapes.

To date, a limited number of studies exist in the literature on the catalytic properties of NPs with different and well-defined shapes. Among others, important contributions to the understanding of the shape-reactivity relationship have been made by the groups of El-Sayed and Narayanan [65,121], Li et al. [122], You et al. [123], and Wang et al. [124]. Different crystallographic facets can be stabilized on particles with different shapes, and different reactivities and selectivities can be obtained on distinct facets. As an example, Xu et al. [122] investigated the oxidation of styrene over cubic, truncated triangular nanoplates, and near-spherical Ag NPs and found the rate of reaction over the nanocube

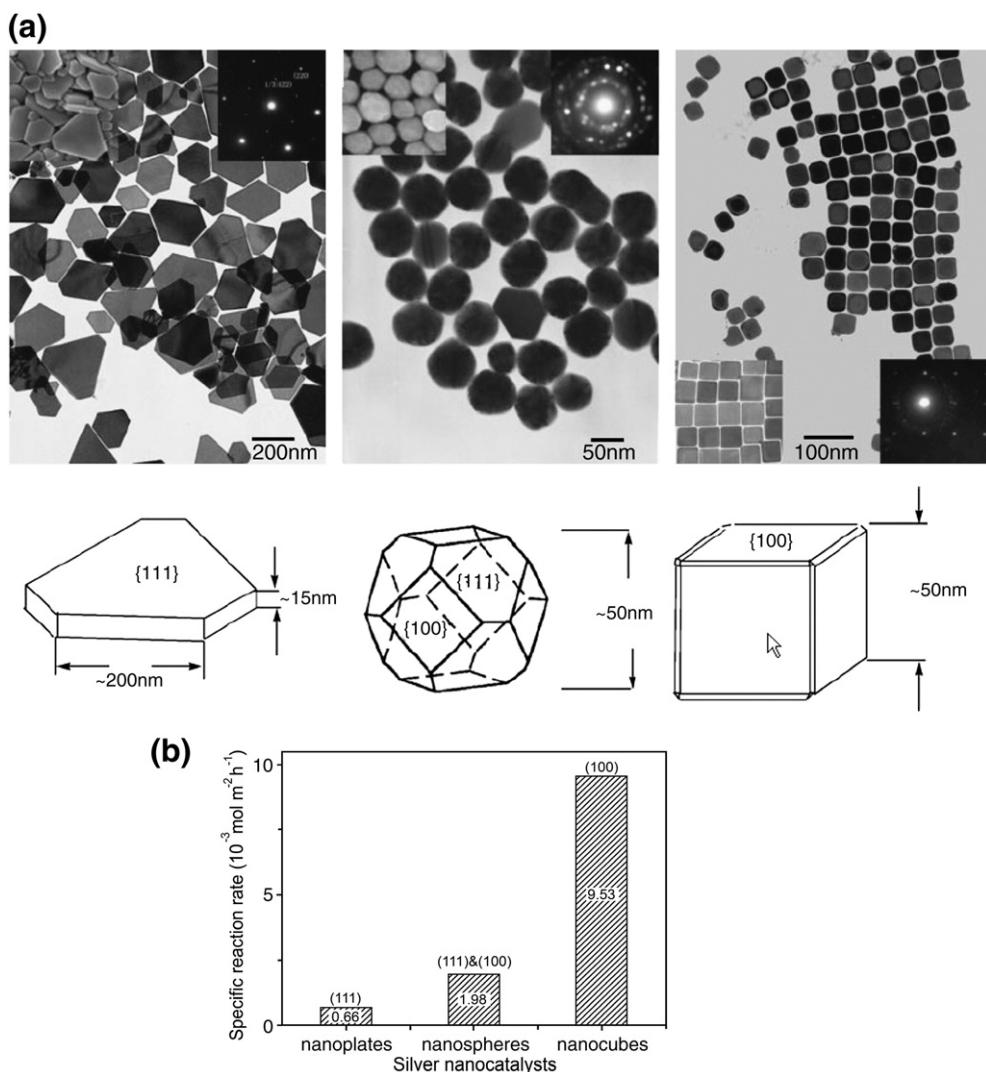


Fig. 12. (a) TEM images of truncated triangular Ag nanoplates (left), near-spherical (middle), and cubic (right) silver NPs supported on Cu-TEM grids and their structural models. The insets show scanning electron microscopy images (top left corner) and electron diffraction patterns from selected areas (top right corner). (b) Specific reaction rate of styrene conversion over Ag NPs with different shapes. Reaction time: 3 h [122].

Xu et al., Chem. Asian J. (2006), 1, 888. Copyright Wiley-VCH Verlag GmbH & co. KGaA. Reproduced with permission.

particles to be fourteen times higher than over the nanoplates, and four times higher than over the nearly-spherical particles, Fig. 12. The authors attributed these differences to the presence of distinct crystalline planes on each of these three systems, with highly reactive {100} facets on the nanocubes, in contrast to the {111} facets present on the nanoplates, and the mixture of {100} and {111} planes in the nanospheres, Fig. 12(a). Tian et al. [124] also reported the enhanced catalytic activity of tetrahedral Pt NPs with high-index facets $\{730\}, \{210\}, \{520\}$ for the electro-oxidation of formic acid and ethanol as compared to equivalent Pt surface areas of NPs with different shapes (e.g. nanospheres), Fig. 13. The authors attributed this finding to the increased number of atomic steps and dangling bonds. Studies by Narayanan et al. [65,121] indicated a faster dissolution of surface Pt atoms on tetrahedral compared to cubic particles during the electron-transfer reaction between hexacyanoferrate (III) and thiosulfate ions. The authors assigned this result to the larger number of low coordinated sites (sharp corners and edges) present in the tetrahedral particles. Komanicky et al. [123] recently illustrated the effect of the particle shape on the oxygen reduction reaction (ORR) over Pt NPs with well defined crystalline orientations prepared by electron beam lithography, Fig. 14 (a). Based on the distinct electrocatalytic activities (e.g. onset potentials) observed for the differently oriented NP arrays, the authors suggested a

synergistic cooperative behavior between (100) and (111) facets for ORR. O_2 is believed to preferentially adsorb on (100) facets, but subsequently diffuse to nearby (111) facets where it is more efficiently reduced, Fig. 14(b).

The above examples illustrate the need for not only having a thorough knowledge of the average cluster sizes and size distribution present in a particular sample, but also the most stable cluster shapes, since both parameters affect chemical reactivity. The work by Frenkel et al. [125] demonstrated the possibility of using spectroscopic tools such as extended X-ray absorption fine structure spectroscopy (EXAFS) in combination with transmission electron microscopy (TEM) and computational modeling to extract such morphological information for supported clusters, Fig. 15. More specifically, the sequence of nearest neighbor atomic distances and coordination numbers extracted from EXAFS measurements was used in Ref. [125] to obtain average cluster diameters assuming different models for cluster shapes. In this study, the most likely shape was concluded by comparing those values to cluster sizes directly measured by TEM.

Recent work by Wang et al. [126], Helveg et al. [127], and Newton et al. [128,129] showed the relevance of probing, in-situ, the composition, electronic and geometric structures of nanocatalysts under reaction conditions. In particular, based on a synergistic combination

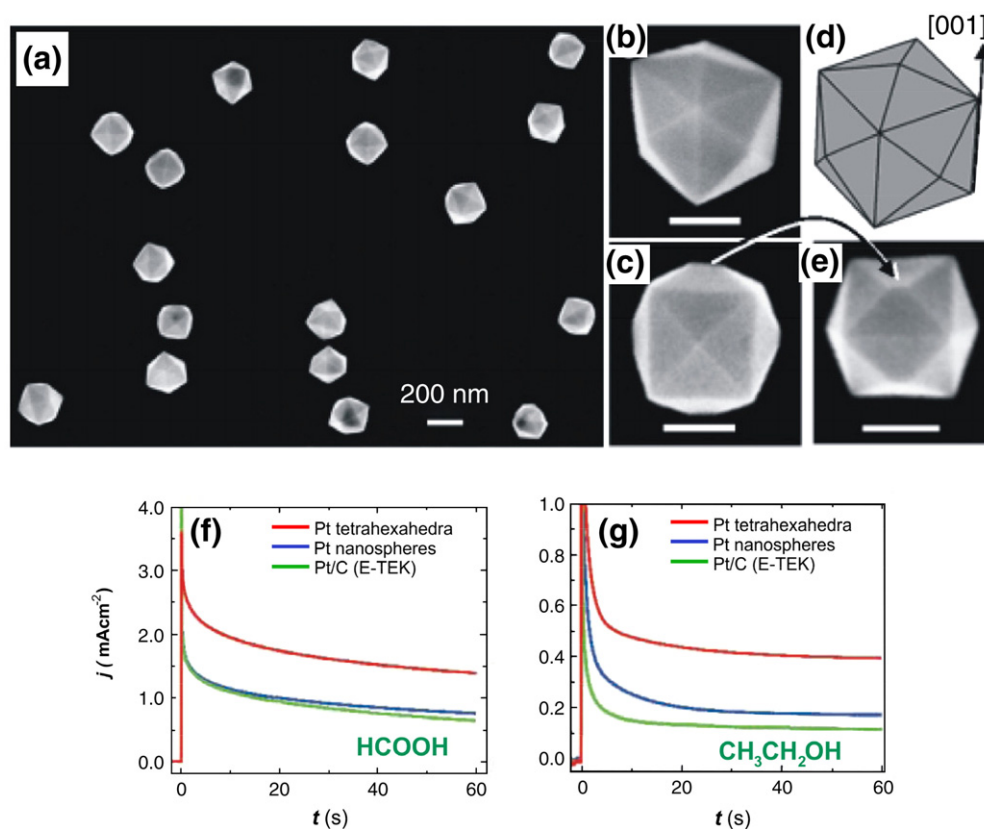


Fig. 13. SEM images of tetrahedral (THH) Pt nanocrystals (NC): (a) low magnification image obtained after a NC growth time of 60 min; (b), (c), and (e) high-resolution images of NCs viewed along different orientations. A geometric model of an ideal THH NC is shown in (d). Scale bars in (b), (c), and (e) are 100 nm. The THH NCs were prepared by an electrochemical treatment of Pt nanospheres supported on glassy carbon with square-wave potentials. A comparison of the catalytic activity per unit Pt surface area among THH Pt NCs, polycrystalline Pt nanospheres, and 3.2 nm Pt/C catalysts is shown in (f) and (g): transient current density curves of formic acid oxidation at 0.25 V (f) and of ethanol oxidation (g) at 0.3 V for differently-shaped Pt nanostructures. The current density (j) was normalized with reference to the electrochemically active surface area for each sample. The superior catalytic activity of the THH NCs is evident.

From N. Tian et al., *Science* 316 (2007) 732. Reprinted with permission from AAAS.

of EXAFS, diffuse reflectance infrared spectroscopy (DRIFTS) and mass spectroscopy, Newton et al. [129] described the dynamical response of supported Pd nanocatalysts to CO/NO cycles in terms of changes of the particle size and shape under the different chemical environments. The effect of O₂ adsorption on the morphology and equilibrium shape of Pd and Rh nanocrystals was investigated theoretically by Mitterdorfer et al. [130]. Their study revealed that although closed-packed (111) facets dominate under low O₂ pressures, nanocrystal rounding occurs at elevated O₂ pressures due to its higher adsorption energy on the initially less stable (110) open surfaces. Grazing incidence X-ray diffraction and TEM experiments by Nolte et al. [131] on Rh NPs supported on MgO(001) indicated an increase in the total area of (100) facets at the expense of (111) surfaces upon oxidation, Fig. 16. Such shape changes were found to be reversible upon subsequent NP reduction during CO oxidation. High resolution TEM images obtained by Giorgio et al. [132,133] under H₂ and O₂ atmospheres (4 mbar) using an environmental TEM demonstrated the faceting of Au NPs supported on TiO₂ under H₂ (truncated octahedron shape), and their rounding and de-wetting under O₂. In analogy to the previous observation on Rh clusters, the latter shape changes also appeared to be reversible.

Chemisorption induced morphological changes in NPs such as the ones described above need to be considered when models to explain catalytic reactivity are proposed, since certain reaction environments might lead to a decrease/increase in the relative area of the most catalytically active surface facets/sites.

6. Support effects

Lack of agreement exists with respect to the role of the substrate on the enhanced catalytic performance of clusters. Hakkinen et al. [104] attributed the distinct catalytic properties of small gold NPs to charge transfer from the metal-oxide support to the NP surface. Experiments by Yoon et al. [20] and Yan et al. [134] on size-selected Au clusters deposited on MgO pointed to the importance of oxygen vacancies (F-centers) in the oxide support in controlling the rate of CO oxidation. DFT calculations by Laursen and Linic [135] suggested that electron charge transfer from O-vacancies at the metal-substrate interface to supported Au nanostructures provides an ideal environment for O₂ activation and oxidation reactions. Further, DFT work by Pillay and Hwang [136] showed that the delocalization of electrons from oxygen vacancies in the reduced TiO₂(110) surface drastically alters the adsorption and surface diffusion of small Au particles. In addition, the electronic structure of these Au particles appeared to be influenced by the transfer of charge from the substrate [136–138]. Recent experimental work by Rodriguez et al. [11,139] also revealed that O-vacancies in CeO₂ supports play a critical role in the decomposition of SO₂ and dissociation of water over Au/CeO₂(111). The rate limiting step in the water-gas-shift (WGS) reaction seems to be the dissociation of H₂O, and this does not occur on perfect CeO₂(111) surfaces or on polycrystalline gold and Au(111) [11]. However, when Au and Cu NPs are deposited on CeO₂(111), the support can be reduced by CO or CO/H₂O mixtures, resulting in an enhanced activity

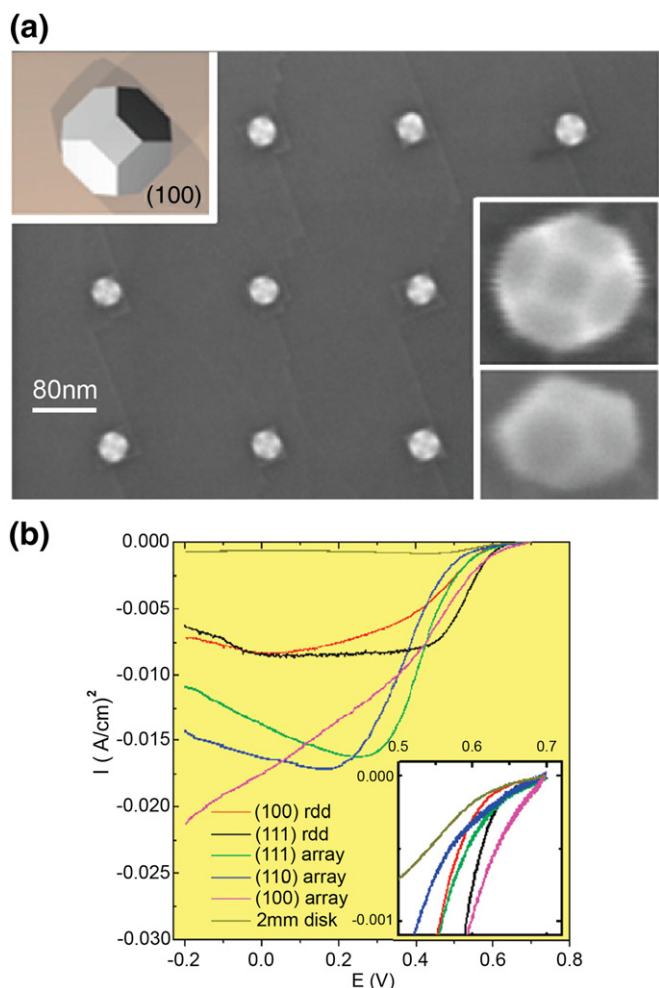


Fig. 14. (a) SEM images of a Pt NP array with (100) crystallographic orientation formed by electron beam lithography (EBL) on $\text{SrTiO}_3(100)$ after annealing at 1450 K. The insets on the right are higher magnification top and side views of a NP, and the one on the left is a model shape resulting from slicing a cuboctahedron along (100). The NP diameter is ~ 30 nm. (b) Oxygen reduction electrocatalytic activity characterized by measuring current–voltage curves in oxygen-saturated 0.1 M perchloric acid. The current densities were obtained by switching the voltage (E) at 50 mV/s in the range of 0.7 V to -0.2 V. The data displayed correspond to three EBL-formed Pt NP arrays with (100), (110), and (111) orientations, together with reference data from a Pt(111) film (labeled as 2 mm disk) as well as Pt(111) and Pt(100) single crystal rotating disks (labeled as rdd). The inset shows a close up of the data. Reprinted with permission from V. Komanicky et al., *J. Am. Chem. Soc.* 131 (2009) 5732. Copyright 2009, American Chemical Society.

for WGS [11], Fig. 17. Further evidence for this conclusion was extracted from the comparison of the Au/CeO₂(111) and Au/ZnO (0001) systems, since the lower activity of the latter system was attributed to the absence of O-vacancy formation under reaction conditions [11]. A recent STM study by Esch et al. [140], at high temperature (900 °C), revealed that the CeO₂(111) surface is not only capable of releasing oxygen atoms, but also trimers, dramatically changing the electronic environment of the remaining cerium ions.

Madix's group [141] studied methanol (MeOH) adsorption on stoichiometric and defective TiO₂(110) surfaces and found that the latter shows a selectivity towards the formation of methane, while the stoichiometric surface does not. Methane formation was attributed to oxygen released from methoxy species healing the anion vacancy defects in the defective surface. Further, studies by Yan et al. [21] revealed that not only the chemical composition, but also the crystal structure (brookite versus anatase TiO₂) of the support, affects the reactivity of the catalyst. Li et al. [142] have also shown that Pt clusters

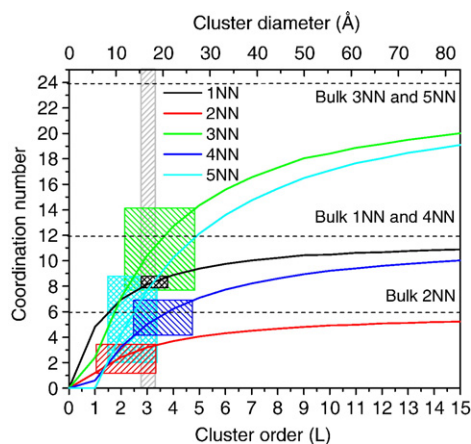


Fig. 15. Cluster shape determination: comparison of the average coordination numbers (with error bars) up to five nearest neighbors (NN) extracted from EXAFS measurements of carbon-supported Pt NPs with those predicted by a model assuming half cuboctahedron hemispherical clusters truncated by a (111) plane. For the latter cluster shape, the sequence of experimentally determined coordination numbers leads to a particle size of ~ 1.7 nm, in fairly good agreement with the average cluster size of ~ 2.4 nm obtained by TEM (not shown). The cluster order (L) is defined as the number of shells around the central atom in a cuboctahedron. Reprinted with permission from A.I. Frenkel et al., *J. Phys. Chem. B* 105 (2001) 12689. Copyright 2001, American Chemical Society.

supported on carbon nanotubes produced a greater power density than when supported on carbon black.

Enhanced catalytic properties for CO oxidation (Figs. 9 and 11) [15,16] and SO₂ dissociation [143] have also been observed when Au NPs are supported on metal carbides such as TiC. In this system, Au–C interactions were found to induce a significant charge polarization around the gold atoms that facilitates the bonding of electron acceptor molecules such as SO₂ and CO [143,144].

The influence of the support on the electronic and structural properties of supported NPs was also demonstrated by Sanchez et al. [145]. In particular, enhanced atomic disorder and the unusual phenomenon of negative thermal expansion were only observed when small Pt NPs were deposited on Al₂O₃, but not on carbon black [145].

Particle supports play an important role, not only by possibly enhancing chemical performance, but perhaps more importantly by stabilizing the supported NPs [83]. Dissolution of Pt in fuel cells can lead to particle agglomeration with a loss of surface area and a decrease in catalyst performance [146]. Data from Croy et al. [25] have shown that MeOH decomposition over Pt NPs is a support-dependent reaction. Different oxide supports were found to show distinct activities and selectivities in this reaction. Among the oxide supports investigated (SiO₂, Al₂O₃, ZrO₂, TiO₂ and CeO₂), ZrO₂ was found to be the best candidate in terms of MeOH conversion efficiency at low temperature and H₂ selectivity, Fig. 18. Acidic sites in this support are believed to be responsible for its superior performance [25]. Surprisingly, although the Pt-free CeO₂ support outperformed the Pt-free ZrO₂, the Pt/CeO₂ catalyst was at the bottom of their performance list. A closer look at these systems at the nanoscale revealed that although Pt NPs with similar sizes were deposited (reverse micelle synthesis) on all supports, the catalyst pre-treatment resulted in significant coarsening on the CeO₂ support, while a good dispersion was observed on ZrO₂, Fig. 18(a). The Pt-NP/ZrO₂ system was also proven by Mostafa et al. [147] to be an active catalyst for the decomposition of high-order alcohols, as is shown in Fig. 19. The onset temperature for alcohol decomposition (H₂ generation) was found to increase from propanol \leq butanol $<$ methanol \leq ethanol, ranging from 125 °C to 200 °C. The maximum alcohol conversion was found to increase from ethanol $<$ 2-butanol \leq 2-propanol $<$ methanol, ranging from $\sim 47\%$ to 100% in a temperature range of 100–300 °C, Fig. 19. High selectivity toward H₂ production was observed for all the

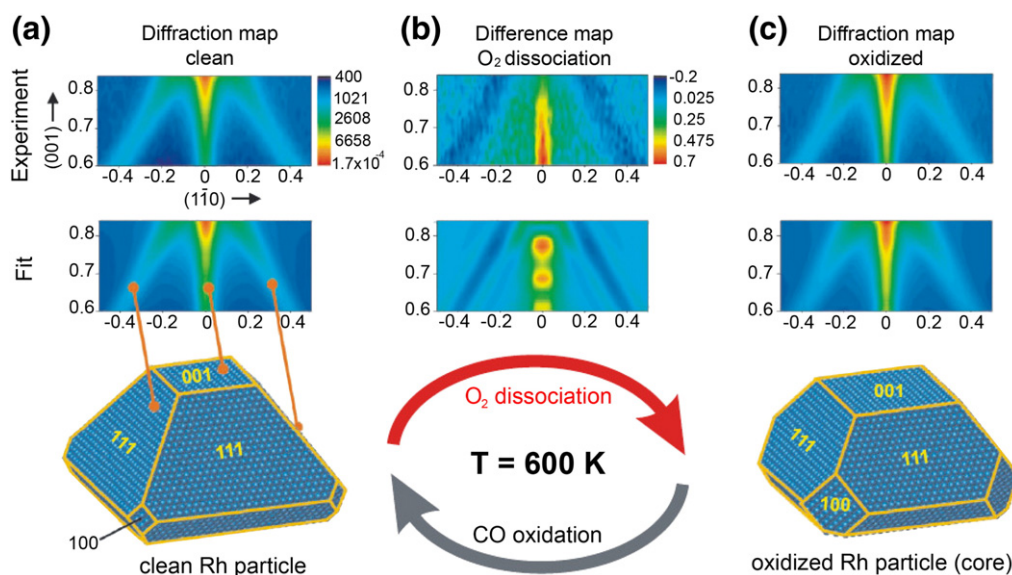


Fig. 16. (Top) Experimental (110) X-ray reciprocal-lattice diffraction maps of Rh NPs taken at 600 K on (a) clean Rh NPs and (c) oxidized Rh NPs under 2×10^{-5} mbar O₂ pressure at 600 K. The NPs were grown epitaxially on MgO(001) at 670 K. The plot in (b) shows the difference in the diffraction signals acquired before and after O₂ exposure. (middle) (a) and (c) Fitted diffraction maps corresponding to the average NP shapes shown below. In (b) the simulated signal change upon O₂ exposure for NPs with an increased (100) side facet area is depicted. From P. Nolte et al., Science 321 (2008) 1654. Reprinted with permission from AAAS.

alcohols being decomposed over the Pt/ZrO₂ catalyst, Fig. 20. With the exception of methanol, all the alcohols studied by Mostafa et al. [147] caused the catalyst to become deactivated at high temperatures ($T > 325$ °C for ethanol and $T > 250$ °C for 2-propanol and 2-butanol) due to the deposition of carbonaceous species over the Pt NPs and their ZrO₂ support. The onset of dehydration reactions, possibly over the ZrO₂ support, was observed following indications of catalyst deactivation during 2-propanol and 2-butanol reactions.

Interestingly, a study by Croy et al. [25] revealed different amounts of Pt-oxide species being stabilized on similarly-sized NPs deposited on the distinct oxide supports. As will be discussed in the following section, the presence of these oxidized Pt species may also affect the performance of the catalysts.

The above section intended to provide the reader with a general overview of the complex interaction between nanoscale catalysts and their supports. The support can affect the reactivity of the overlying NPs in several different ways: (i) by stabilizing the NPs against coarsening (enhanced lifetime), (ii) by changing the structure and shape of the NPs (2D versus 3D), (iii) by encapsulating the active NPs at elevated temperatures (undesired effect), (iv) by means of charge

transfer to or from the NPs, (v) by providing additional reaction sites (e.g. oxygen vacancies), (vi) by contributing to the stabilization of metal oxides at the NP surface and NP/support interface that may play an active role (oxygen reservoir) in oxidation reactions, and (vii) by stabilizing intermediate reaction species. It is not possible to predict in a general way which of these factors will be dominant in heterogeneous catalytic reactions, and it should be clear by now that one cannot simply neglect the NP support, especially when a thorough

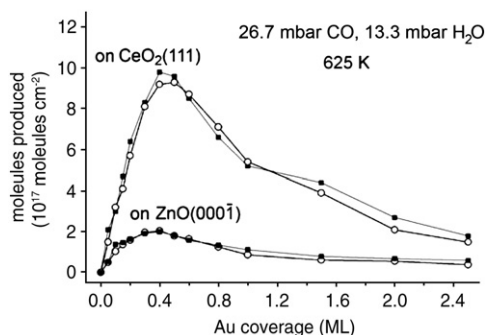


Fig. 17. Relative amounts of H₂ (solid squares) and CO₂ (open circles) produced during the WGS reaction on Au/CeO₂(111) and Au/ZnO(0001) catalysts. The particle sizes are in the range of 2–4 nm. Each surface was exposed to a mixture of 20 Torr CO and 10 Torr H₂O at 625 K for a period of 5 min in a batch reactor. A reaction time of 2–3 min was enough to reach a steady-state regime in the reactor [11]. J.A. Rodriguez et al., Angew. Chem. Int. Ed. (2007) 46, 1329. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

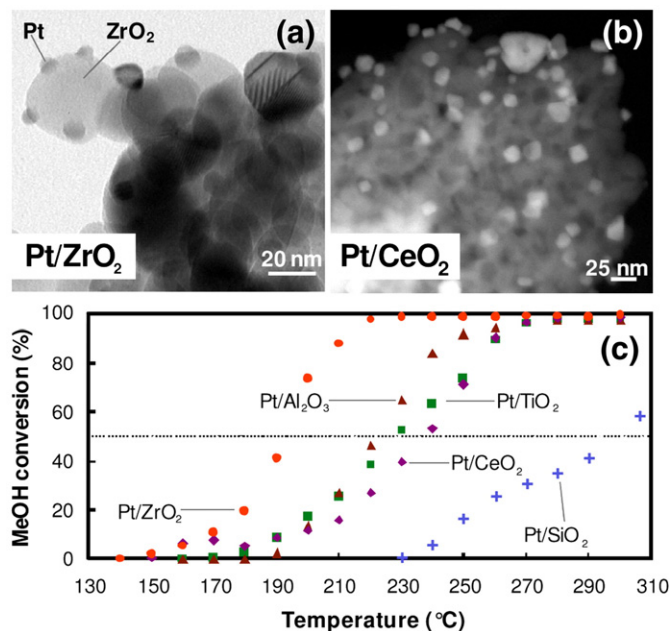


Fig. 18. (a) TEM image of Pt NPs supported on nanocrystalline ZrO₂. (b) High angle annular dark field image obtained by scanning transmission electron microscopy (STEM) of Pt NPs deposited on CeO₂. (c) Relative conversion during the direct MeOH decomposition over Pt NPs supported on Pt/ZrO₂ (full circles), Pt/Al₂O₃ (full triangles), Pt/TiO₂ (full squares), Pt/CeO₂ (full diamonds), and Pt/SiO₂ (crosses). All the oxide supports are nanocrystalline. With kind permission from Springer Science + Business Media: Catal. Lett. 119 (2007) 209, J.R. Croy et al.

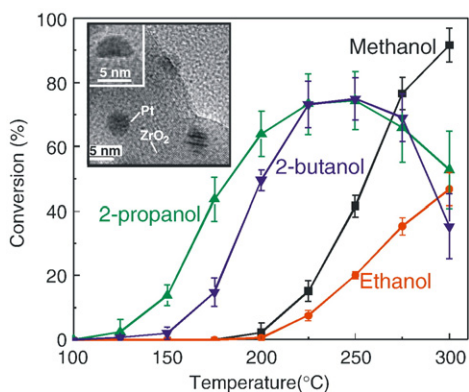


Fig. 19. Temperature-dependent relative alcohol conversion data obtained in a packed-bed mass-flow reactor interfaced to a mass spectrometer during the direct decomposition of methanol, ethanol, 2-propanol, and 2-butanol. The data correspond to Pt micellar NPs deposited on nanocrystalline ZrO_2 . The inset displays a representative TEM image of these samples.

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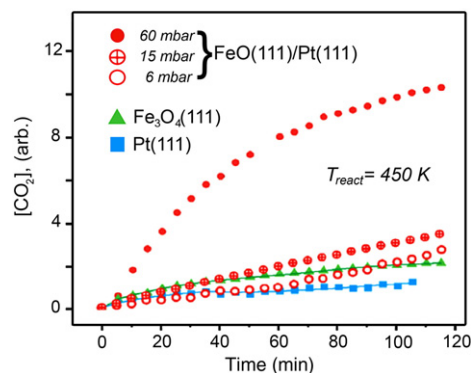


Fig. 21. Kinetics of CO_2 production over $FeO(111)/Pt(111)$ for $CO:O_2$ (2:1) ratios at 60 mbar, 15 mbar, and 6 mbar and 450 K reaction temperature. For comparison, data from a $Pt(111)$ crystal and $Fe_3O_4(5\text{ ML})/Pt(111)$ are also shown.

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understanding of the origin of the catalytic reactivity of supported NPs is desired.

7. Oxidation State effects

Although the majority of industrially viable reactions are conducted on NPs oxidized under the reaction conditions, not much information is currently available on how the oxidation state of these catalysts affects their reactivity. This problem has generated renewed interest after recent findings by Over et al. [106] indicated that under O_2 -rich conditions and moderate temperatures, the $Ru(0001)$ surface first oxidizes to form RuO_2 , and CO oxidation actually occurs not on the metal surface, but on the oxide [18,148–150]. A similar effect was observed for CO oxidation on Pt [151,152], in which case it was suggested that the reactivity of $PtO_2(110)$ was higher than that of a Pt metal surface. In addition to PtO_2 , PtO and Pt_3O_4 species have also been reported to be active for CO oxidation reactions over various Pt films and single crystal surfaces [153–157]. Gong et al. [158,159] compared calculated CO oxidation energetics and pathways for $Ru(0001)$, $Rh(111)$, $Pd(111)$, $Os(1000)$, $Ir(111)$, $Pt(111)$ and their corresponding oxides [$RuO_2(110)$, $RhO_2(110)$, $PdO_2(110)$, $OsO_2(110)$, $IrO_2(110)$, and $PtO_2(110)$] and concluded that the oxides are indeed more reactive than metals. Recent work by Friend's group on O-covered $Au(111)$ also demonstrates the enhanced reactivity of the pre-oxidized gold surface [160,161]. PdO compounds are also considered the active catalytic species for CH_4 and C_3H_8 oxidation as well as reactions with volatile organic compounds [162–164]. Very recently, investigations by Sun et al. [165] also revealed a high reactivity of monolayer-thick iron oxide films grown on $Pt(111)$ for low temperature CO oxidation, Fig. 21. Surprisingly, such films were found to be more active than nm-thick $Fe_3O_4(111)$ films and clean $Pt(111)$ crystals. The origin of the enhanced reactivity of the ultrathin FeO_x films is still under investigation, but it appears to be related to the presence of a metal substrate underneath, suggesting the importance of electron transfer processes at metal oxide/metal interfaces.

It thus appears that the traditional negative view of oxidation as a process leading to reduced catalytic performance must be reconsidered [166]. The results noted above on the oxidation of a metal surface, and its subsequent role in promoting reactivity of the surface, have led to a change in the research paradigm for the area. For example, it has stimulated the development of reliable computational approaches designed to bridge the materials, pressure and temperature gap in theoretical modeling of catalysis and chemical reactions [167].

While the effects of pre-oxidation on the catalytic activity of metal surfaces are the subject of extensive studies, much less is known about such phenomena on supported NPs. Experimentally, this is largely due to the challenge of fabricating reproducible samples with consistent

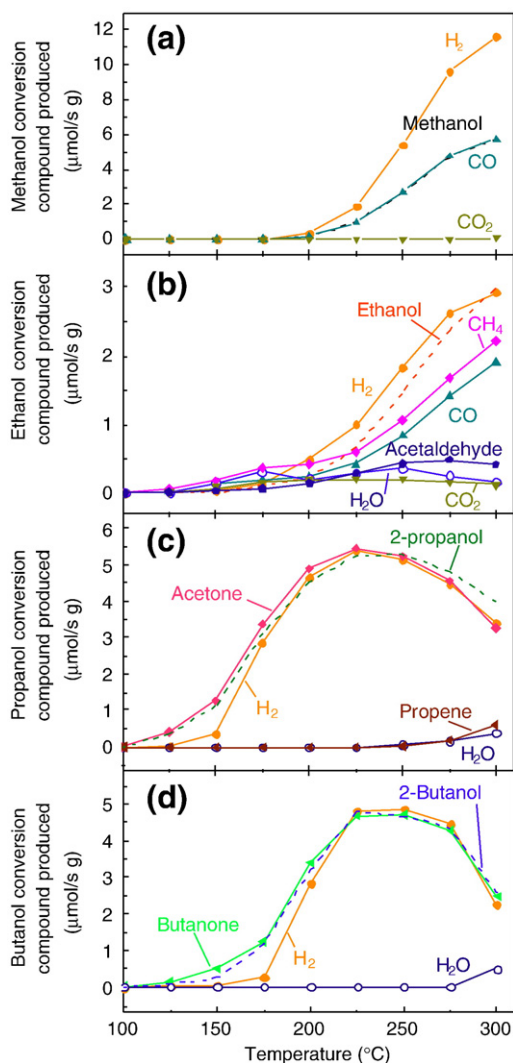


Fig. 20. Rate of alcohol decomposition (dashed lines) and production of related by-products over Pt NPs supported on nanocrystalline ZrO_2 (solid lines and closed symbols). The data correspond to (a) methanol, (b) ethanol, (c) 2-propanol, and (d) 2-butanol decomposition. The rates are normalized by the weight of Pt/ZrO_2 catalyst in each sample ($\sim 0.1\text{ g}$).

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particle size, shape, and oxide stoichiometry. Despite this challenge, the catalytic properties of several metal oxide NPs including RhO_x [168], Fe_2O_3 [169], CoO , TiO_2 [170], NiO [171,172], Cu_2O [173], and PdO_2 have been studied. Computational studies by Huber et al. [27] found that pre-oxidation of Pd NPs adsorbed on MgO dramatically enhances their activity towards CO oxidation. They showed that CO_2 is formed by association of CO and O belonging to the PdO_x cluster. On Pd NPs supported on Fe_3O_4 , Freund's group [28] found that Pd oxide is preferentially stabilized at the particle/oxide-support interface, and that such interfacial films can act as efficient oxygen reservoirs for surface reactions. Huber et al. [27] also highlighted that the oxide support plays an important role in the oxidation of metal NPs by lowering the activation energy barrier. Such reaction mechanisms are bound to be quite sensitive to the pre-oxidation kinetics, which themselves are complex phenomena. For example, while some surfaces oxidize directly from the chemisorbed state [Ni(001) and Al(111)] [159], others such as Ag(111), Cu(111), Pd(111), Pt(111) and Ni(110) [174–178], form an intermediate surface oxide prior to the formation of the passivating oxide film. The pioneering work of Thürmer et al. [179] has also drawn attention to the corrosion behavior displayed by NPs. STM studies from this group showed that ultrapure Pb clusters exposed to high doses of O_2 were resistant towards oxidation. However, when traces of surface impurities were available, the oxidation of Pb was initiated at even lower O_2 pressures. The working hypothesis here is that oxidation requires the presence of atomic O and highly mobile metal atoms on the surface. The impurities in Thürmer's samples may act as active sites for the dissociation of O_2 . In a related work, Boyen et al. [180] found a non-monotonic size-dependency in the oxidation behavior of Au NPs exposed to atomic oxygen. In particular, Au_{55} clusters (1.4 nm) were found to be resistant to oxidation. However, it is not clear if this effect can be simply attributed to size-dependent changes in the electronic structure of the NPs.

Although for some metal oxides, such as RuO_2 , there is already a thorough understanding of the nature of their enhanced reactivity [106,166,181], and superior catalytic performance over their metallic counterparts is generally agreed upon, the same cannot be said for other important catalytically active metals such as Pt. In the latter case, there is an ongoing debate in the current literature as to whether Pt oxides are beneficial or detrimental to the catalytic performance of Pt particles. Gastgeier et al. [182] have attributed the decay in the performance of fuel cell electrodes to the formation of PtO. Thus, the resistance to oxidation that can be achieved by alloying Pt with noble metals could be of advantage for this system. In this respect, Zhang et al. [183] have shown that Pt surfaces modified with Au clusters are stable under highly oxidizing conditions. Metallic Pt species were also reported to be the most active species for C_3H_8 combustion [184] and NO_2 decomposition [185]. For example, the improved catalytic activity of Pt deposited on acidic supports observed by Yazawa et al. [184] was attributed to the support's ability to preserve the metallic state of Pt [184]. Olsson et al. [185] discussed the effect of the cluster support on the oxidation state of Pt in terms of the different NP dispersions achieved, since the smaller NPs were found to be more oxidized. Interestingly, such small clusters had the lowest associated chemical reactivities. However, other authors claim enhanced activity and stability of Pt particles covered by PtO_x shells [25,186–189]. As an example, Dam et al. [186] reported that Pt dissolution in fuel cells reaches a saturation level due to the presence of a protective platinum oxide layer. An entirely opposite result had been previously published by Ferreira et al. [146]. Fu et al. [188] attributed the activity of Pt-NP/ CeO_2 catalysts during the water-gas shift reaction to the presence of ionic (Pt^{2+} , Pt^{4+}) Pt species, and the same appears to be true for CO oxidation reactions.

Croy et al. have observed that the size [24], the catalyst pre-treatment [76], the support [25], and the secondary metal [187] of mono- and bimetallic Pt catalyst can influence the type of oxide

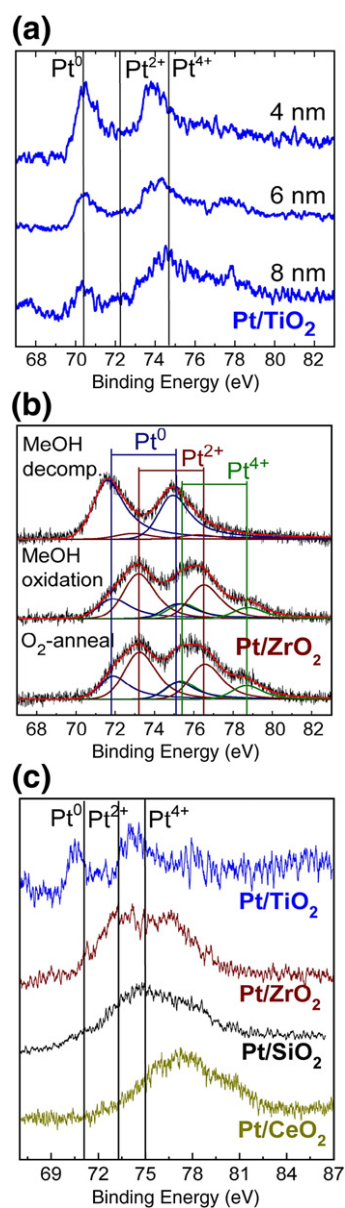


Fig. 22. Pt-4f core level XPS spectra ($\text{Al-K}_{\alpha} = 1486.6$ eV) of (a) differently-sized Pt NPs (4 nm, 6 nm, and 8 nm) deposited on nanocrystalline TiO_2 , (b) Pt NPs of identical size distribution supported on ZrO_2 before and after exposure to methanol oxidation and decomposition reactions, and (c) Pt NPs deposited on nanocrystalline TiO_2 , ZrO_2 , SiO_2 , and CeO_2 . The samples in (a) and (c) were annealed at 500°C in air prior to the measurements, while those in (b) were annealed at 500°C in O_2 prior to MeOH exposure. The large Pt-4f binding energies observed for the Pt/ CeO_2 system (c) is not due to the presence of Pt-oxides, but to the formation of Pt-Ce alloys at 500°C upon the partial reduction of CeO_2 . The vertical lines indicate the binding energies of the Pt-4f_{7/2} core level of metallic Pt, PtO, and PtO₂ species.

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formed (PtO, PtO₂) as well as the stability of the metal-oxide shell present on “real world” catalysts under realistic reaction conditions. PtO and PtO₂ species were detected in these samples by XPS after annealing treatments in air and O_2 from 300°C to 500°C . For a given substrate (TiO_2), the smallest NPs investigated (4 nm) were found to be the easiest to reduce, Fig. 22(a) [24]. Further, significant reduction of Pt oxides was observed on Pt-NP/ ZrO_2 catalysts during MeOH decomposition reactions (with the CO produced here acting as reducing agent), while the same species were preserved during

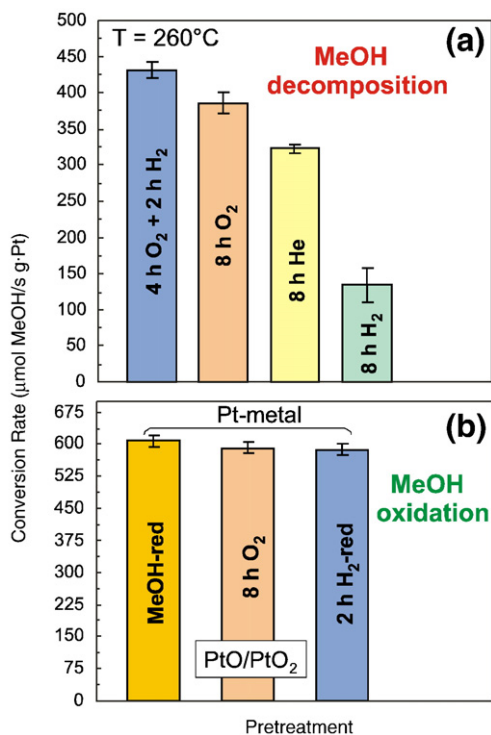


Fig. 23. Rate of (a) MeOH decomposition at 260°C and (b) MeOH oxidation at 50°C for Pt/ZrO₂ samples given in $\mu\text{mol}(\text{MeOH})/\text{s g Pt}$. Pretreatments applied to each sample are listed. Each pretreatment and reaction was conducted on a separate, fresh sample. With kind permission from Springer Science + Business Media: Catal. Lett. 131 (2009) 21, J.R. Croy et al.

MeOH oxidation reactions [76], Fig. 22(b). Interestingly, none of the pre-treatments described in Ref. [76] (including prolonged annealings in H_2 up to 500°C) resulted in the complete removal of PtO_x species from these Pt/ZrO₂ nanocatalysts, signaling the possible formation of interfacial Pt–O–Zr compounds. In addition, an enhanced stability of the Pt oxide species was observed when the NPs were deposited on non-easily-reducible oxide supports (e.g. SiO₂, ZrO₂) as compared to, for example, TiO₂, Fig. 22(c) [25]. The presence of Pt-oxides formed during different pretreatments on the surface of Pt NPs was found to have little influence in methanol decomposition reactions, Fig. 23(a), due to their high tendency to reduce, Fig. 22(b) [76]. No appreciable difference in the activity of the latter catalysts for MeOH oxidation was observed while comparing oxidized versus reduced samples, Fig. 23(b) [76]. This is evidence that the oxidized surfaces of these Pt NPs (most likely disordered and defective) are active for the oxidation of MeOH, and reduction pre-treatments commonly reported in the literature may not be necessary. Furthermore, the oxidized surface appears to take part in a Mars-van Krevelen-type of process, exchanging oxygen from the particle's Pt oxide shell with gas-phase O₂, allowing it to remain oxidized during/after MeOH oxidation reactions, Fig. 22(b) [76]. A similar process was previously observed by Westerström et al. [190] during the oxidation of CO over Pt₂₅Rh₇₅ (100) catalysts, with an increased CO₂ production occurring in parallel to the formation of a thin RhO₂ surface oxide film. In this example, the oxide film consumed during the reaction is continuously re-grown by gas-phase O₂.

The stability, activity, and selectivity of Pt and its oxides in response to interactions with potential fuels are areas of great importance that presently deserve further attention. With the ever increasing industrial use of nanomaterials, their impact on the environment has become an issue of great importance. Specifically, thermally or mechanically induced emissions of particulate Pt from automobile catalytic converters is a source of toxicological concern [191–195]. Therefore, not only is the

performance of the working catalysts important, but so also is the state in which they might be emitted into the environment upon reaction (oxidized, chlorinated, etc.). Although catalysts are prepared in a certain state (i.e. Pt⁰), it has been shown that the oxidation state of the working catalyst might be different, and how this state evolves and reacts under environmental conditions might be of concern.

Despite the fact that bulk gold is known as one of the most inert metals in the periodic table [196], oxidized gold compounds can be formed on gold single crystals [77,197,198], polycrystalline thin films [199,200], and supported gold NPs [75,115,180,201,202] upon exposure to reactive oxygen species (e.g. O₂-plasma or ozone treatments). In analogy to the case of Pt, lack of consensus still prevails with respect to the chemical state of the active species in gold NPs [188,203–209], as well as the relative importance of the different oxygen species (chemisorbed oxygen, surface oxide, subsurface oxygen or bulk oxide) that might be present on these catalysts under working reaction conditions [206,207,210,211]. For example, the active role of cationic gold species in the water–gas shift reaction has been proposed by Fu et al. [188]. In this work, similar activities for the WGS reaction were obtained for gold NPs supported on La-doped CeO₂ before and after the removal of the metallic gold species [188]. This result suggested a strong interaction of ionic gold with the ceria support, and the authors claimed that the presence of metallic gold species was not necessary for this catalytic reaction. On the other hand, near-edge X-ray absorption fine structure spectroscopy (NEXAFS/XANES) data by Rodriguez et al. [212] suggested that Au^{δ+} species are not stable under WGS reaction conditions ($P_{\text{CO}} = 20$ Torr, $P_{\text{H}_2\text{O}} = 10$ Torr, $T = 575\text{--}650$ K), and can therefore not be responsible for the enhanced reactivity of the Au NP/CeO₂ system. However, DFT calculations by Liu et al. [213] indicated that empty, localized nonbonding *f*-states in CeO₂ could facilitate the oxidation of Au and enable subsequent CO adsorption. Several other groups have used DFT to investigate the strength of the binding of CO [214–217], O₂ [217–221], propene [222], and methanol (MeOH) [223] to non-metallic Au clusters. Here, a common trend was found with reactant molecules showing stronger binding energies to anionic and cationic gold species, as compared to metallic gold. Further, calculations by Okumura et al. [224] suggested that although O₂ activation occurs on anionic Au, cationic Au atoms bind CO stronger. The authors proposed a model of dynamic charge polarization in which a strong heterojunction between Au clusters and their support is indispensable for the activation of oxygen species. The presence of negatively charged atoms in the perimeter region of Au NPs was attributed to localized Coulomb blockade effects. Furthermore, this surface negative charge was found to increase with decreasing cluster size [224], in agreement with the known enhanced catalytic activity observed for small Au clusters.

Recently, a number of experimental studies have been published on the chemical reactivity of gold surfaces pre-covered with atomic oxygen [160,161,225–227]. Min et al. [160] reported the existence of three types of oxygen species on Au(111): (i) chemisorbed oxygen (oxygen bound to gold that is not part of an ordered phase), (ii) oxygen in surface oxide (well-ordered two-dimensional phase), and (iii) subsurface oxygen or bulk oxide (three dimensional phase). Interestingly, the relative stability of surface versus subsurface gold oxide was found to depend on the sample temperature during atomic oxygen exposure. Further, based on CO oxidation studies, the authors found that chemisorbed oxygen and surface gold oxide species were more reactive than bulk gold oxide [160]. The role played by these species in the thermodynamics and kinetics of oxidation/reduction reactions is a major challenge for the microscopic understanding of gold catalysis. This understanding becomes highly challenging when small NPs are considered, due to the added complexity of the presence of different facets, kinks and steps, and the interactions with the support [115,201].

Recent studies by Ono et al. [115] showed that the stability of gold oxide on supported gold clusters depends on the cluster size and nature of the cluster support. Their work demonstrated that low temperature (150 K) exposure to atomic oxygen leads to the

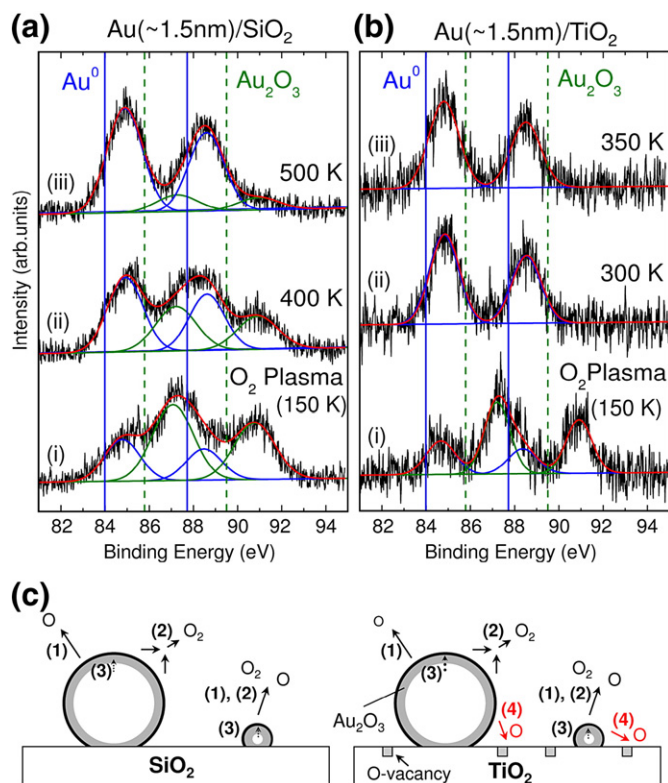


Fig. 24. XPS spectra (Al K_{α} = 1486.6 eV) corresponding to the Au-4f core level of Au NPs with an average size of ~ 1.5 nm supported on nanocrystalline (a) SiO₂ and (b) TiO₂. The temperature-dependent spectra shown follow the decomposition of Au oxide after UHV annealing from 200 to 500 K (10 min). (c) Schematic model illustrating different mechanisms for Au₂O₃ decomposition on large and small NPs supported on SiO₂ and TiO₂. Four processes are depicted: (1) direct desorption of atomic oxygen, (2) recombination of atomic oxygen and desorption as molecular oxygen, (3) segregation of subsurface oxygen to the NP's surface, and (4) atomic oxygen from the NP shell spills over to the TiO₂ substrate and replenishes oxygen vacancies created on TiO₂ upon sample annealing. Reprinted with permission from L.K. Ono and B. Roldan Cuenya, *J. Phys. Chem. C* 112 (2008) 4676. Copyright 2008, American Chemical Society.

formation of surface, as well as sub-surface gold oxide on Au NPs of two average sizes (~ 1.5 and ~ 5 nm) deposited on SiO₂ and TiO₂. The effect of the substrate was evidenced by a reduced stability of gold oxide on Au NPs supported on TiO₂, a system where strong metal-support interactions are expected, Fig. 24(a), (b) [115]. The authors suggested oxygen spill-over from the cluster's oxidized surface shell to O-vacancies formed in the reducible TiO₂ substrate upon annealing as a possible gold oxide decomposition pathway, Fig. 24(c). Nearly complete reduction of the small (~ 1.5 nm) gold NPs was observed at 300 K for Au/TiO₂ and at 550 K for Au/SiO₂. In contrast, for larger clusters only partial Au₂O₃ decomposition was observed up to 600 K. This suggested that at least on the large NPs, two different oxygen species were present: surface gold oxide that decomposes at temperatures below 600 K in vacuum, and bulk or subsurface oxide that is stable well above 600 K. For the small NPs, the presence of surface and subsurface oxide was confirmed by CO dosing experiments [115]. A decrease in the Au³⁺ XPS signal and an increase in Au⁰ upon CO exposure indicated the reduction of surface gold oxide. The observation of incomplete Au³⁺ reduction for CO dosings as large as 9000 L provided clear evidence for the presence of stable subsurface gold oxide species in all samples. Although both NP size and support were found to influence the stability of Au₂O₃, the support effect is more pronounced, as evidenced by a very fast reduction of Au³⁺ in Au/TiO₂, and enhanced gold oxide stability in Au/SiO₂.

As was mentioned above, the stability of oxygen species over metal surfaces is of interest in the field of catalysis due to their possible

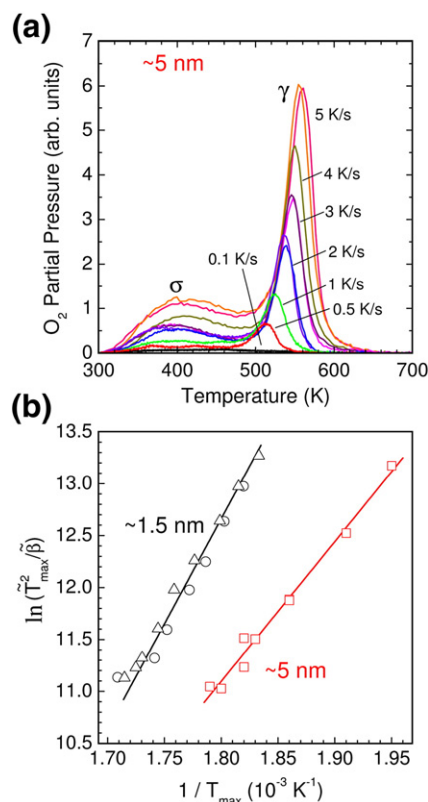


Fig. 25. (a) Series of O₂ TPD spectra obtained on ~ 5 nm Au NPs deposited on SiO₂/Si(111) after exposure to a constant initial O coverage of 0.22 ML. The heating rate β was varied from 0.5 to 5 K/s. (b) $\ln(T_{\max}^2/\beta)$ versus $1/T_{\max}$ plots obtained from the heating rate variation data displayed in (a) for ~ 5 nm NPs (open squares) and similar data acquired on ~ 1.5 nm NPs (open triangles and circles). Reprinted with permission from L.K. Ono and B. Roldan Cuenya, *J. Phys. Chem. C* 112 (2008) 18543. Copyright 2008, American Chemical Society.

involvement in catalytic oxidation reactions [177,178,228–230]. A number of studies can be found in the literature [231–240] reporting kinetic parameters of O₂ desorption from Au single crystal surfaces with different orientations after atomic oxygen exposure. Nevertheless, a range of desorption energies ($E_d = 1.0$ – 1.5 eV) as well as first- and second-order pre-exponential factors ($\nu_1 = 8 \times 10^9 \text{ s}^{-1}$ – $6 \times 10^{13} \text{ s}^{-1}$ and $\nu_2 \sim 10^{13} \text{ ML}^{-1} \text{ s}^{-1}$) have been reported [231,234–237,241] based on TPD measurements. These differences can be attributed to the distinct initial adsorbate coverages (θ_0) used [235,237] and coverage-dependent adsorbate–adsorbate interactions [238], to specific interactions of oxygen with different Au surface terminations, as well as to intrinsic limitations of the particular TPD analyses methods employed.

Fewer studies exist on the reaction kinetics of O₂ desorption from complex systems such as supported Au NPs [115,118,239,240], and further insight is needed on how the particle size and NP-support interface might affect these kinetics. By using size-selected micellar Au NPs as a model experimental system, Ono and Cuenya [118] have recently demonstrated that the desorption temperature of O₂ from pre-oxidized Au NPs deposited on SiO₂ depends on the NP size, with smaller NPs showing stronger oxygen binding, Fig. 25(b). Thanks to their sample preparation route, they were able to measure desorption parameters on much more monodispersed particle size distributions than previous studies, and determine how such parameters evolve as a function of particle size. More specifically, desorption energies of ~ 1.3 and ~ 1.7 eV were obtained for Au NP/SiO₂ samples with average sizes of ~ 5 nm and ~ 1.5 nm, respectively. Their results are in agreement with previous data by Campbell's group [239,240], where ~ 1.44 eV and ~ 1.70 eV were obtained for 6-atom and

2-atom high Au islands, respectively, deposited on TiO₂, ruling out support effects from the trend observed in the desorption energy. Furthermore, the work by Ono and Cuenya [118] also evaluated the validity of different TPD analysis methods to extract reliable desorption energies and pre-exponential factors from supported NP samples [118], highlighting the uncertainties of background subtraction procedures when desorption signals originating from the metal NPs and their supports overlap.

The above influence of the oxidation state of a catalyst on its reactivity might be better understood once a more profound knowledge of how an elemental process such as O₂ adsorption affects catalyst structure becomes available. For example, for Al₂O₃-supported Pt cluster sizes <2 nm, TEM and X-ray absorption spectroscopy data (XAS) from Sanchez et al. [145] revealed a decrease in the Pt–Pt bond-lengths due to O₂ adsorption, while the opposite effect, together with an attenuation of the structural disorder, was observed upon H₂ adsorption. Furthermore, with the continuous development of ultrafast timing capabilities in the new generation of synchrotron sources, additional opportunities for in-situ monitoring of reaction intermediates in real time are arising. An example of the validity of XAS measurements combined with principal component analysis for the determination of the structure and chemical specification of intermediate oxide species during the in-situ reduction of Cu-doped ceria can be found in Ref. [126].

Summarizing, the presence of surface and interfacial oxides on supported nanocatalysts should be taken into consideration when models describing catalytic reactivity are proposed based on UHV experiments or calculations, since such species are certainly present in the majority of “real-world” nanocatalysts under reaction conditions. Their role in catalysis is still not fully understood and likely need

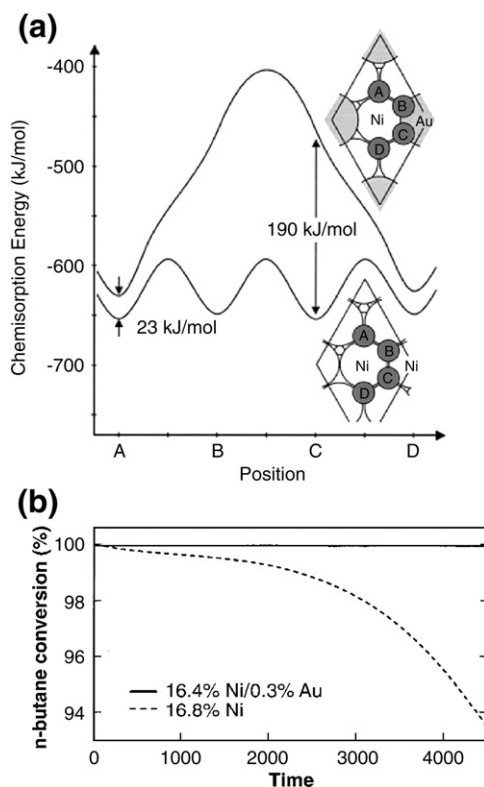


Fig. 26. (a) DFT calculated adsorption energy of a C atom on different Ni(111) sites (bottom curve) and on the same Ni surface after replacing one Ni atom by a Au atom (top curve). The insets display the surface geometry in both examples. (b) Conversion of n-butane as a function of time during steam reforming (3% C₄H₁₀/7% H₂/3% H₂O in He at a space velocity of 1.2 h⁻¹) for Ni (dashed curve) and Au/Ni supported catalysts (solid curve). The space velocity is defined as the relation between the volumetric flow and the reactor (or catalyst bed) volume. From F. Besenbacher et al., Science 279 (1998) 1913. Reprinted with permission from AAAS.

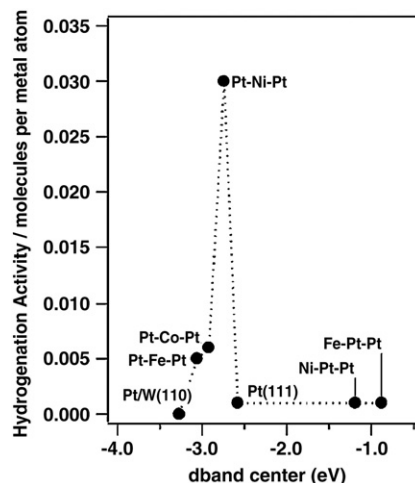


Fig. 27. Hydrogenation activity of cyclohexene as a function of the position of the d-band center for a series of Pt–M–Pt and M–Pt–Pt sandwich layer model catalysts [260]. M.P. Humbert et al., Chem. Phys. Chem. (2008), 9, 1262. Copyright Wiley-VCH Verlag GmbH & co. KGaA. Reproduced with permission.

to be investigated on a case-by-case basis. However, some experimental evidence already exists on the active role of several metal oxide species for oxidation reactions.

8. Composition effects

The need of promoters or multimetallic catalytic systems has emerged due to several factors, including reducing the price of the active catalysts and increasing their activity, selectivity, and long-term stability. As an example, in order to make direct methanol fuel cells (DMFC) [242,243] more economically viable, the amount of Pt in the cells is being decreased by alloying with less expensive metals that might in turn also help to enhance the activity at the electrodes [244,245], as

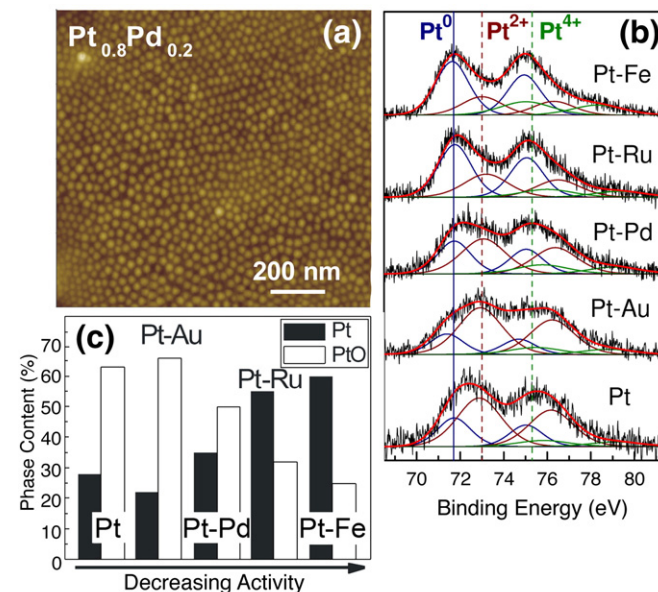


Fig. 28. (a) AFM image of Pt₈₀Pd₂₀ NPs synthesized by micelle encapsulation and deposited on SiO₂/Si(111). (b) XPS spectra (Al K_α = 1486.6 eV), acquired after annealing in air at 500 °C, from the Pt-4f core level region of size-selected Pt₈₀M₂₀ (M = Au, Pd, Ru, and Fe) NPs supported on nanocrystalline ZrO₂. (c) Relative content of metallic Pt (solid bars) and PtO (open bars) obtained from the analysis of the XPS data shown in (b). Reprinted from Appl. Catal. A, 350, J.R. Croy et al., 207, Copyright 2008, with permission from Elsevier.

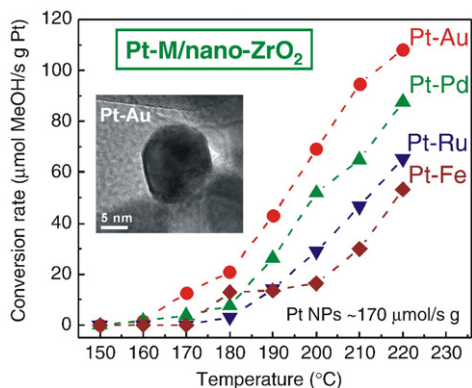


Fig. 29. Temperature-dependent rate of methanol conversion obtained from mass spectroscopy data over $\text{Pt}_{0.8}\text{M}_{0.2}$ ($\text{M} = \text{Au}, \text{Pd}, \text{Ru}, \text{and Fe}$) NPs supported on nanocrystalline ZrO_2 . The insert shows a high-resolution image of a PtAu NP. Reprinted from Appl. Catal. A, 350, J.R. Croy et al., 207, Copyright 2008, with permission from Elsevier.

well as the resistance to poisoning caused by the byproducts associated with the use of alcohols as a fuel [246]. Other examples are Ba-promoted Ru catalysts, that are currently among the most active catalysts for ammonia synthesis [247], and Au–Ni surface alloys (top-most-layer) as

stable steam reforming catalysts [248]. In the latter case, the addition of Au to Ni surfaces does not result in a lower barrier for hydrocarbon activation (e.g., CH_4), and therefore higher reactivity, but in the decreased stability of adsorbed C on Ni, Fig. 26(a). This effect minimizes the subsequent formation of graphite, preventing thus catalyst deactivation processes, Fig. 26(b).

In order to take advantage of bimetallic systems in the design of new catalysts, the structural, chemical, and electronic modifications induced by the addition of the secondary metal need to be fully understood [116,181,248–261]. Of particular relevance are the changes in the electronic structure of metal surfaces brought about by the formation of bimetallic bonds (ligand effects) as well as by the modification of metal–metal bond lengths (strain effects). Several mechanisms are believed to be responsible for the enhanced catalytic performance of certain bimetallic systems, including charge-transfer phenomena between the different metals in a multimetallic system that may favorably change the binding energy of adsorbates [257,262–264], the presence of lower barriers for specific chemical reactions [262], and improved resistance against poisoning and subsequent deactivation [248,265].

In the case of Pt, alloying with metals such as Fe, Ru, Ni, Co, as well as others, has been reported to enhance their hydrogenation [260,266–268] and oxygen reduction reaction (ORR) activities [251,269,270], as well to enhance resistance to CO poisoning [271]. The effectiveness of Ru and Au secondary metals to minimize the poisoning effects of MeOH oxidation reactions over Pt surfaces has been demonstrated [272–274]. In particular, it has been suggested that Ru provides preferential sites for OH adsorption, which are then responsible for the oxidation to CO_2 of the residues from alcohol chemisorption, thus preventing the accumulation of poisoning species such as CO [246]. The optimum Ru content in the

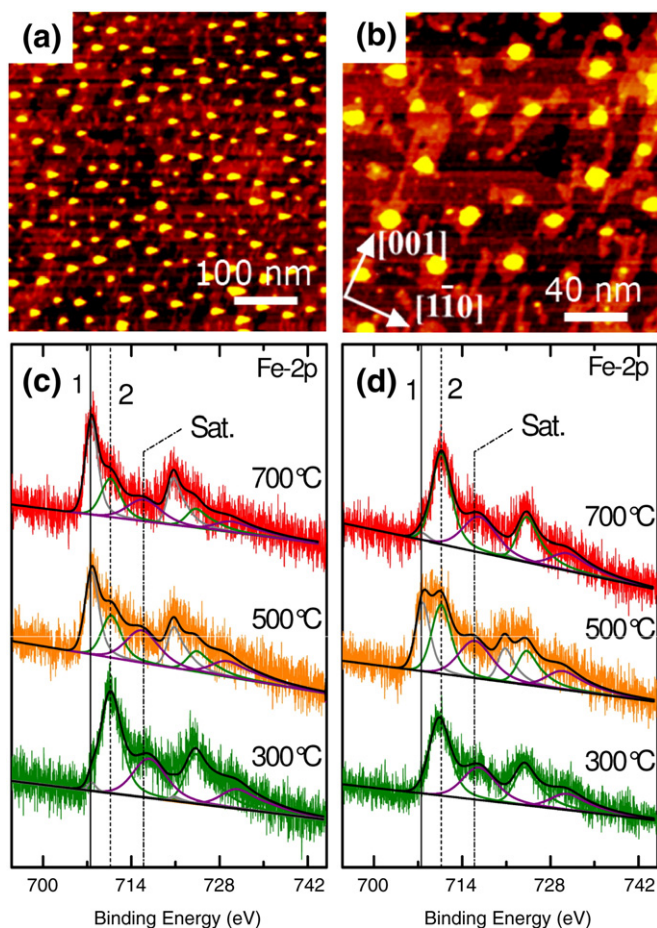


Fig. 30. (a) and (b) STM images of $\text{Au}_{0.5}\text{Fe}_{0.5}$ NPs, acquired at two different magnifications, synthesized by inverse micelle encapsulation and supported on $\text{TiO}_2(110)$. The images were obtained after O_2 -plasma treatment and sample annealing in UHV at 900°C for 20 min. XPS data ($\text{Al K}_{\alpha} = 1486.6 \text{ eV}$) from the Fe-2p core level region of (c) pure Fe NPs and (d) $\text{Au}_{0.5}\text{Fe}_{0.5}$ NPs supported on $\text{TiO}_2(110)$ after annealing in UHV at the temperatures indicated. Reprinted with permission from A. Naitabdi et al., J. Phys. Chem. C 113 (2009) 1433. Copyright 2009, American Chemical Society.

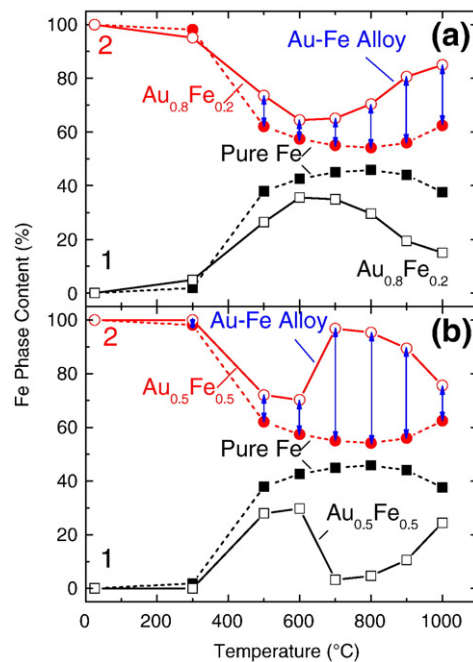


Fig. 31. Evolution of the relative content (spectral area) with annealing temperature of the two different Fe phases (component 1 and component 2 in Fig. 30) obtained from the fits of Fe-2p XPS spectra acquired after sample annealing in UHV from RT to 1000°C . The data shown correspond to (a) $\text{Au}_{0.8}\text{Fe}_{0.2}$ and (b) $\text{Au}_{0.5}\text{Fe}_{0.5}$ NPs (open squares and open circles connected by solid lines). For comparison, the phase content of the pure Fe NPs is also plotted (solid squares and solid circles connected by dashed lines). The component labeled as 1 (squares) corresponds to metallic Fe ($\text{Fe-}2p_{3/2}$ at $706.9\text{--}707.7 \text{ eV}$), while component 2 is assigned to Fe-oxides + $\text{FeTiO}_{3+\delta}$ compounds + Au–Fe alloy ($\text{Fe-}2p_{3/2}$ at $709.8\text{--}712.2 \text{ eV}$ and satellites at $\sim 720 \text{ eV}$). The vertical arrows indicate the increase in the phase content of component 2 (Au–Fe alloy) relative to the phase content of component 1 (metallic Fe). Reprinted with permission from A. Naitabdi et al., J. Phys. Chem. C 113 (2009) 1433. Copyright 2009, American Chemical Society.

alloy is still a topic of investigation and a Pt/Ru alloy is not necessarily the best catalyst for use with other fuels. Pt/Sn alloys have been shown to enhance activity for the oxidation of ethanol [218], and Au/ α -Fe₂O₃/Pt catalysts for the oxidation of ethylene glycol [275]. However, few studies of this kind have been done for other alcohols. Gupta et al. [276] have shown that 2-propanol does not form bound intermediates at undoped Pt surfaces, thereby inhibiting poisoning. Recent experimental and theoretical studies by Chen's group [260] demonstrated the superior hydrogenation properties of Pt–Ni–Pt sandwich structure catalysts as compared to Ni–Pt–Pt, Fig. 27. In this work, a correlation between the location of the surface d-band center with respect to the Fermi level and the reactivity of catalysts with different structures was established. The latter electronic parameter was used to gain insight into the binding of certain adsorbates to surfaces, including H, O and small alkenes. The presence of Ni atoms at the surface of layered catalysts (Ni–Pt–Pt) was

found to induce a shift in the d-band center towards the Fermi level, what results in a stronger adsorbate binding. When the Ni atoms were present below the surface (Pt–Ni–Pt), the contrary trend was observed, resulting in weaker adsorbate binding and unexpected low-temperature hydrogenation activities. Nevertheless, an optimum binding energy is required, since weak binding was found to prevent alkene hydrogenation [260], Fig. 27. Such synergistic experimental and computational model system investigations can provide guidance for the rational formulation of novel catalysts.

In the above studies, the surface properties of the alloys are credited with the observed catalytic improvements, and the nature of the secondary metal, as well as the preparation and pretreatment conditions, are known to have a large influence over the final composition and

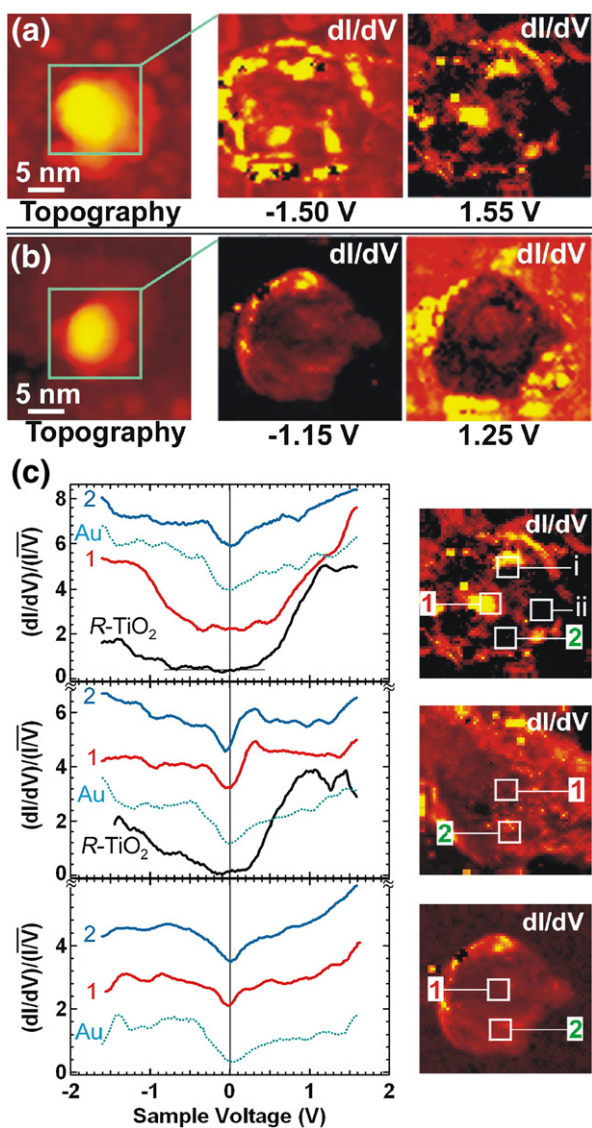


Fig. 32. STM images (topography) and normalized dI/dV STS maps of two different Au_{0.5}Fe_{0.5} NPs supported on TiO₂(110); measured after O₂ plasma treatment and annealing at (a) 300 °C and (b) 900 °C. dI/dV maps are recorded using a (64 × 64) grid over an area of 12.5 × 12.5 nm² (light blue squares). (c) Normalized differential conductivity curves acquired on the above NPs after O₂ plasma and annealing at 300 °C (top), 700 °C (center), and 900 °C (bottom). Inserts on the right are dI/dV images indicating the position of the acquisition grids used. Each curve was obtained from the average of 64 individual I – V curves taken over different (1.5 × 1.5) nm² regions inside each NP. Dotted curves were obtained on a reference sample containing pure Au NCs of similar size deposited on TiO₂(110) and annealed at identical temperatures. Adapted from Naitabdi et al. [116].

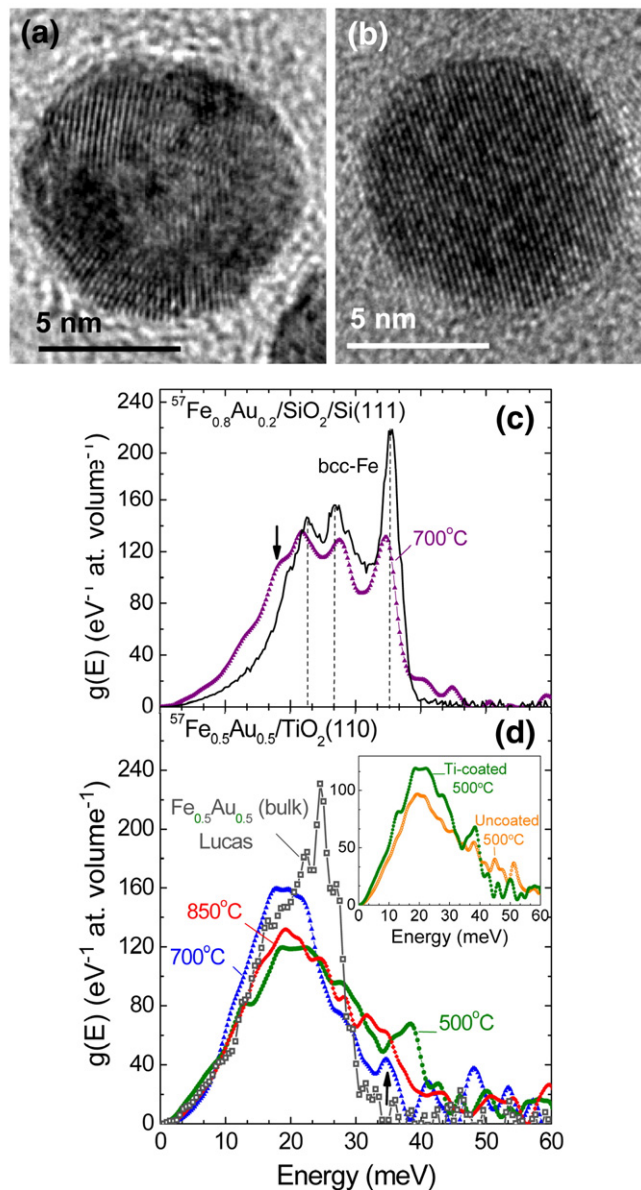


Fig. 33. High resolution TEM images of ⁵⁷Fe_{0.5}Au_{0.5} NPs on Ti-coated Ni grids. All images were obtained after polymer removal by an O₂-plasma treatment followed by annealing in UHV at (a) 700 °C and (b) 900 °C. Fe-projected phonon density of states, $g(E)$, of: (c) ⁵⁷Fe_{0.8}Au_{0.2} NPs on SiO₂/Si(111) and (d) ⁵⁷Fe_{0.5}Au_{0.5} NPs on TiO₂(110) after O₂-plasma treatment and annealing in UHV at (d) 500 °C, (c and d) 700 °C, and (d) 850 °C for 30 min. The NPs in (c) are uncoated and in (d) protected by a 5-nm Ti layer. For reference, $g(E)$ of bulk bcc Fe is shown in (c) and bulk Fe_{0.5}Au_{0.5} alloy from Ref. [329] in (d). The inset in (d) displays $g(E)$ of uncoated and Ti-coated ⁵⁷Fe₅₀Au₅₀ NCs annealed at 500 °C. Adapted from Roldan Cuenya et al. [278].

oxidation state of the active surface components. For example, Croy et al. [187] recently reported a change in the stability of PtOx species on size-selected Pt_{0.8}M_{0.2} NPs supported on ZrO₂ depending on the affinity for oxygen of the secondary metal (M = Au, Pd, Ru and Fe), Fig. 28. In addition, the preferential segregation of metals that form stable oxides (Fe, Ru, and Pd) to the NP surface in these Pt–M systems during calcination pre-treatments in air was observed, and its effect on the NP's catalytic activity for methanol decomposition discussed. In the latter study, all Pt–M samples showed lower reactivity than pure Pt, Fig. 29. This was explained by the occupation of surface sites by metal M atoms, since pure Au, Fe, Pd, and Ru clusters supported on ZrO₂ were found to be less reactive for MeOH decomposition than similarly-sized pure Pt clusters [187]. The role of the distinct initial content of Pt oxides in the Pt–M NPs in their reactivity was considered to be negligible, since XPS data from the same group revealed the prompt reduction of such species during alcohol decomposition reactions [76,187].

Despite recent positive progress, additional investigations of the effect of the chemical and thermal environments on segregation phenomena as well as changes in the oxidation state of multi-component nanoscale systems are still needed, since this type of understanding is a requirement for the rational design of efficient catalysts. In order to determine reliable correlations between alloy composition and chemical reactivity of NPs, synthetic approaches that provide size-selected clusters with homogeneous compositions are required. Fair progress has been made in the past in terms of achieving bimetallic NP samples with narrow size distributions, Fig. 30(a), (b), but challenges still remain with respect to the composition homogeneity. This is of particular importance since at present the majority of the techniques commonly used to obtain quantitative information on NP composition in multimetallic systems provide ensemble-averaged data [see for example XPS data from AuFe NPs in Figs. 30(d) and 31].

In order to obtain an accurate picture of such multimetallic systems, ensemble-averaged spectroscopic tools such as ultraviolet photoelectron spectroscopy (UPS), XPS, EXAFS and others should be complemented by NP-specific sampling techniques including transmission electron microscopy/energy dispersive X-ray spectroscopy (TEM-EDX) and STM-STs (Fig. 32). For example, in-situ XPS measurements were used in Ref. [119] to follow the formation of Au–Fe alloys and surface segregation processes in micellar Au_xFe_{1-x} NPs supported on TiO₂(110). With increasing annealing temperature, several NP structures were inferred based on changes in the Fe-2p core level binding energy region, including the presence of segregated Fe and Au grains in the as-prepared samples, a heterogeneous mixture of Au–Fe alloy (majority phase) plus a minority Fe phase at $T \geq 600$ °C, and an Fe-rich core with a Au-rich surface at $T > 800$ °C, Figs. 30 and 31, [119]. These results are in agreement with previous local STM-STs measurements from the same group [116] on Au_{0.5}Fe_{0.5} NPs that revealed the presence of isolated Au and Fe₂O₃ grains

(oxidized Fe upon NP exposure to atomic O) at 300 °C, Fig. 32(a) (top) and (c) (top), and the formation of a AuFe alloy upon annealing at 700 °C (characterized by the appearance of an iron $d_{3z^2-r^2}$ electronic surface state at 0.25 V), Fig. 32(c) (middle). The subsequent segregation of Au to the NP surface at 900 °C was inferred by the disappearance of the Fe surface state observed at 700 °C, Fig. 32(b) and (c) (bottom). Naitabdi et al. [119] also demonstrated the high thermal stability of Au in Au_{0.8}Fe_{0.2} NPs (up to 1000 °C) compared to pure Au, Au_{0.5}Fe_{0.5}, and Au_{0.2}Fe_{0.8} NPs of similar average size, from which Au was found to desorb above 900 °C. Molecular dynamics simulations by Mottet et al. [277] revealed a considerable upward shift in the melting temperature of icosahedral Ag clusters when Ni and Cu impurities were introduced. This effect was attributed to the release of stress in the NP core due to the presence of Ni and Cu. A similar effect might explain the enhanced thermal stability of our Au_{0.8}Fe_{0.2} NPs.

In addition, our group has recently demonstrated the validity of isotopic-specific methods such as nuclear resonant inelastic X-ray scattering (NRIXS) for the investigation of alloy formation and segregation phenomena at the nanoscale [278,279]. In particular, the phonon density of states extracted from NRIXS measurements provides important information on the structure of bimetallic NPs and its evolution as a function of the relative content of the different elements as well as of the annealing temperature. Such information is complementary to the structural information resulting from TEM measurements, Fig. 33(a), (b). For example, the change in the structure of ⁵⁷FeAu NPs from bcc-like for ⁵⁷Fe₈₀Au₂₀ NPs to fcc-like for ⁵⁷Fe₅₀Au₅₀ NPs is shown in Fig. 33(c), (d) [278], where phonon density of states (PDOS) data from bulk bcc-Fe and a bulk Fe₅₀Au₅₀ alloy are also shown for reference. Corresponding theoretical modeling, including MD studies, are needed in order to fully understand the origin of the enhanced thermal stability of certain bimetallic NP compositions as well as to get insight into adsorbate-induced changes in their structure.

In summary, among other obvious benefits such as a decrease in the cost of the catalytically active elements (Pt, Au, etc.), the use of alloys in NP catalysis can result in: (i) decreased poisoning effects, (ii) the opening of new reaction pathways leading to distinct selectivities, (iii) the enhancement of catalytic activity due to synergistic effects and changes in the electronic properties of the nanocatalysts, and (iv) an improved thermal stability of the catalytically active elements.

9. Outlook and future research directions

Since the definition of the concept of *catalyst* given by Berzelius in 1836 (“soluble and insoluble simple and compound bodies that have the property of exercising on other bodies an action very different from chemical affinity, and that remain unaltered through the reaction”) [280], the field of catalysis has experienced an astonishing transformation. This change has been driven in part by more demanding

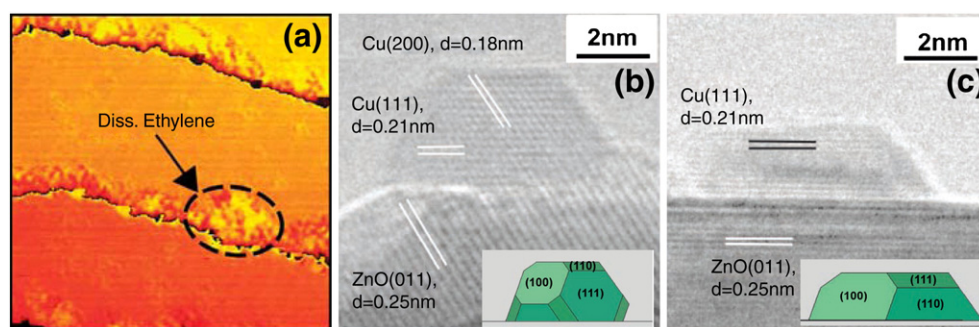


Fig. 34. (a) STM image (200 Å × 200 Å) of a Ni(111) surface after 1 L exposure to ethylene at room temperature. The circled region highlights reaction products nucleated along the upper step edges. (b) and (c) In-situ TEM images of Cu/ZnO catalyst obtained under different conditions: (b) a pressure of 1.5 mbar of H₂ at 220 °C, and (c) a gas mixture of H₂ (95%) and CO (5%) at a total pressure of 5 mbar at 220 °C. The insets show the corresponding Wulff constructions for the Cu nanocrystals. Panel (a) was taken from Vang et al. [287]. From P.L. Hansen et al., Science 295 (2002) 2053. Reprinted with permission from AAAS.

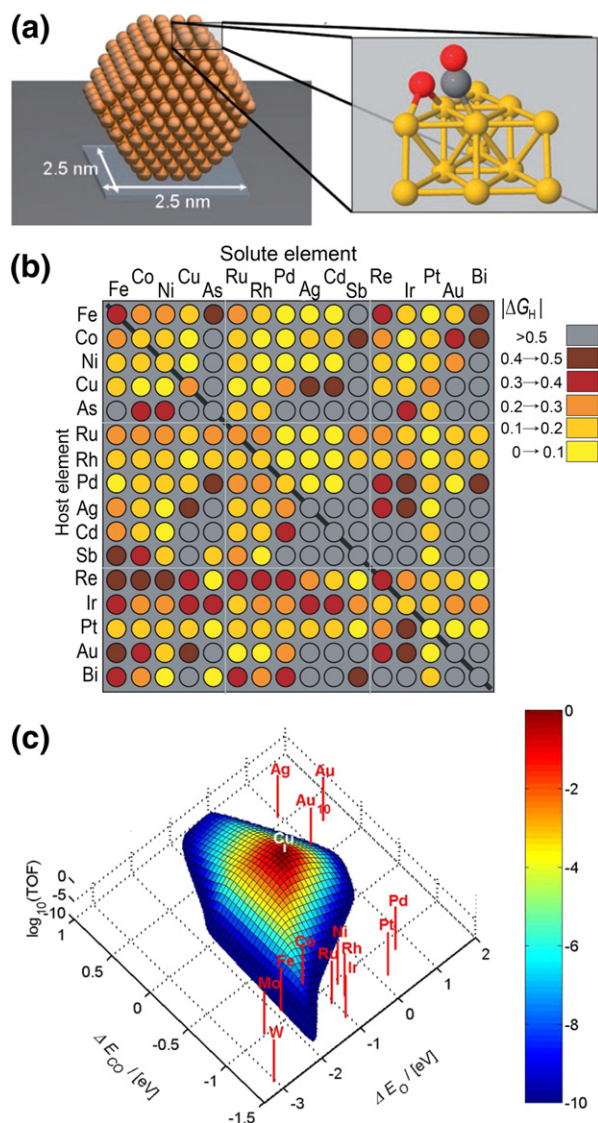


Fig. 35. (a) Model of a cuboctahedral Au NP (2–3 nm) (left) and representation of the transition state for CO oxidation on a 12-atom cluster by Falsig et al. [314], *Angew. Chem. Int. Ed.* (2008), 47, 4835. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. In the schematic, molecular O_2 has already been dissociated and only one oxygen atom remains on the surface. The red atoms correspond to atomic oxygen and the gray ones to carbon monoxide adsorbed on undercoordinated Au atoms (right) [315]. (b) Computational screening results for the hydrogen evolution reaction (HER). Each circle represents a binary surface alloy and the color represents the hydrogen adsorption free energy, $|\Delta G_H|$, calculated by DFT. The highest predicted catalytic activities for HER are indicated by lighter colors. (c) Calculated turnover frequencies of the water-gas-shift (WGS) reaction as a function of carbon monoxide and oxygen adsorption energies. The chemisorption energies at step sites of noble and late transition metals are marked. The 3D plot reveals that copper is the only pure metal well-suited as a catalyst for the WGS process, which is in agreement with current experiments. Panel (a) Grabow and Mavrikakis, *Angew. Chem. Int. Ed.* (2008), 47, 7390. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. Panel (b) was reprinted by permission from Macmillan Publishers Ltd: *Nature Mater.* 5 (2006) 909, copyright 2006. Panel (c) was Reprinted from *J. Catal.*, 229, N. Schumacher et al., 265, copyright 2005, with permission from Elsevier.

environmental standards and industrial (pharmaceutical, power generation, etc.) needs. Thanks to the advent of nanotechnology, major steps forward have been made toward the rational design of novel catalysts. With the continuous decrease in the length scales of the material systems of interest (from single crystal surfaces to thin films, nanoparticles, and molecular clusters), the need for more sensitive in-situ microscopic and spectroscopic tools and computational approaches

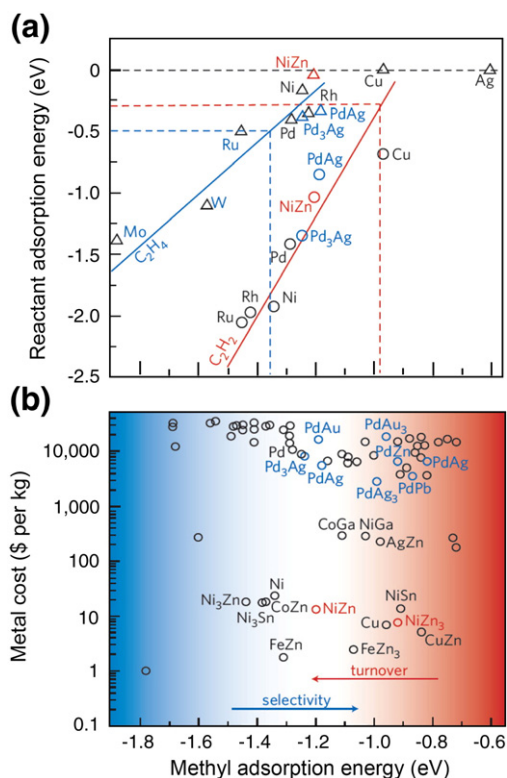


Fig. 36. Demonstration of the advantages of using computer designed catalysts for the selective acetylene hydrogenation. (a) Heats of adsorption of acetylene (C_2H_2) and ethylene (C_2H_4) as a function of the heat of adsorption of methyl (CH_3) [same x-axis values as in (b)] over several pure metals and their alloys. Linear scaling relations for acetylene (red) and ethylene (blue) adsorption are indicated by solid lines. The dotted blue line indicates the maximum methyl binding energy for which C_2H_4 is predicted to desorb instead of hydrogenating to ethane. The dotted red line defines the minimum methyl binding energy necessary to obtain a turnover frequency on the order of 1 s^{-1} . Both lines define a methyl binding energy region in which a given catalysts is active and selective. (b) Plot of the cost in dollars (in 2006) of 70 binary intermetallic compounds as a function of the calculated methyl adsorption energies calculated. The experiments verify the theoretical prediction that NiZn catalysts can exhibit selectivity (zero ethane) comparable to that of PdAg [288,325]. From F. Studt et al., *Science* 320 (2008) 1320. Reprinted with permission from AAAS.

that can be operated across a wide range of temperature and chemical environments and real time has arisen. These new needs should be addressed in the years to come. Present research directions are abandoning the concept of static catalysts and adopting the more realistic vision of a dynamical entity that might be subject to structural, morphological, and chemical changes in the course of a reaction. In order to be able to monitor such changes, in-situ (“in-vivo”) observations of catalysts at work [131–133], with ideal single-molecule single-nanoparticle sensitivity, should be carried out. Some examples of how the above philosophy has been and is currently being put forward, including recent progress trying to bridge the materials and pressure gap experimentally [Fig. 34], and the theoretical size-, complexity-, temperature- and pressure-gaps [Figs. 35 and 36] can be found in Refs. [40,46,123,128–130,145,151,152,260,281–307].

On the theoretical side, the development of massive parallel computing technology and recent advances in physical simulation algorithms for detailed geometric and electronic structure investigations [308–313] are contributing to an improved understanding on the factors that influence chemical reactivity at the nanoscale. Although ab-initio calculations of relatively large nanoscale systems (hundreds to thousands of atoms) are still very time consuming and in many cases unachievable, it is presently possible to derive models to describe simple reactions over small NPs (tens of atoms) that can be representative of

the more realistic 2–6 nm experimental systems. An example is the CO oxidation reaction over Au NPs [314,315], Fig. 35(a). In this archetype case, previous experiments have indicated that the most catalytically active sites are undercoordinated Au atoms, rendering models involving small NPs with a large number of such sites relevant to understanding of reaction pathways.

The powerful new computing infrastructures are starting to close the gap between theoretical and experimental work in the fields of nanoscience and nanocatalysis [260,268,314–320]. The ultimate goal is to obtain a molecular-scale picture of the mechanisms underlying surface chemical reactivity [321] that would allow us to accurately predict the performance of a catalyst exclusively based on computer models, without the need for extensive trial-and-error experimental screening, so-called “computational catalysis” [288,322]. For example, computational screening methods were used to evaluate more than 700 bimetallic alloys as possible hydrogen evolution catalyst candidates, Fig. 35(b). Only a few candidates were selected as suitable for experimental testing, and among those, a BiPt alloy was experimentally shown to display superior activity over pure Pt [323]. Another example is the work of Schumacher et al. [324] demonstrating that Cu is the only pure metal well-suited as a catalyst for the WGS process based on calculations of CO and O₂ adsorption energies on step sites of a variety of mono and bimetallic catalysts, Fig. 35(c). Work by Norskov's group [288,325] also illustrates the advantage of having predictive computational capabilities applied to the field of heterogeneous catalysis. The example shown in Fig. 36 corresponds to the selective hydrogenation of acetylene (C₂H₂) to ethylene (C₂H₄) [288,325]. Here, a catalyst is considered to perform adequately when two factors concur: (i) a high adsorption energy for C₂H₂ is observed, and (ii) the adsorption energy of C₂H₄ is small, preventing it from further hydrogenating to the unwanted C₂H₆ byproduct instead of desorbing.

One of the major future applications of nanoscale catalysts will be for power generation purposes. Fuel cells have been intensively studied since their inception in 1839 by Sir William Robert Grove [326]. They are now widely accepted as the next step in power generation for many applications including commercial power and portable electronic devices. In recent years, economic, environmental, and political concerns have pushed fuel cells and their application to transportation to the forefront of scientific research. Despite the vast effort put forth to this end, there remains considerable room for improvement based on a fundamental understanding of the chemical processes involved and the rational selection of novel materials [327,328]. Due to the storage issues associated with hydrogen, several alcohol fuels are being considered as alternatives for use in fuel cell vehicles. Fuels such as methanol and ethanol are among the leading candidates due to their adaptability to the existing infrastructure. Ethanol in particular has already been produced from biomass for many years on a large scale in Brazil and is currently sold for use in conventional automobiles.

Regardless of the intended application, the common challenge of achieving long lasting, highly active, selective, and environmentally friendly catalytic materials and processes still remains. Significant progress is still required for the design of efficient catalysts based on abundant elements (Fe, Si, Ti, C, etc.) in order to replace the scarce and expensive noble metals (Pt, Au, Ir, etc.) presently employed in a number of industrial catalytic processes. Nanoscience approaches are expected to help in this respect. In addition, more satisfactory experimental and theoretical approaches that minimize trial and error experiments in the process of new catalysts development should be put forward. Lessons are still to be learned from catalysts readily available in nature (e.g. enzymes), and the activities of heterogeneous catalysts should be brought to the level of their homogeneous counterparts. This will only be possible through a synergistic interaction of theoretical and experimental groups, the latter taking advantage of the next generation of in-situ analysis tools.

Acknowledgment

The author is grateful to the members of her research group, Dr. Luis Ono, Jason Croy, Simon Mostafa, and Farzad Behafarid (UCF) for their dedication to some of the research described above, as well as to Prof. Werner Keune (Univ. Duisburg-Essen) for stimulating discussions. Funding from the US Department of Energy, Office of Basic Energy Sciences (DE-FG02-08ER15995) and the National Science Foundation (NSF-CAREER 0448491) is greatly appreciated.

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