

## In-Situ Studies of Nanocatalysis

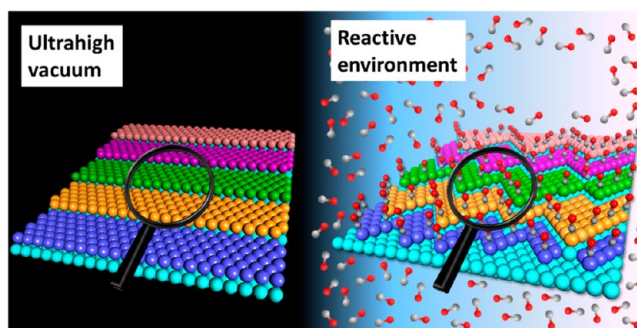
SHIRAN ZHANG,<sup>†</sup> LUAN NGUYEN,<sup>†</sup> YUAN ZHU,<sup>†</sup> SIHUI ZHAN,<sup>†</sup>  
CHIA-KUANG (FRANK) TSUNG,<sup>\*,‡</sup> AND FRANKLIN (FENG) TAO<sup>\*,†</sup>

<sup>†</sup>*Department of Chemistry and Biochemistry, University of Notre Dame,  
Notre Dame, Indiana 46556, United States, and* <sup>‡</sup>*Department of Chemistry,  
Boston College, Chestnut Hill, Massachusetts 02467, United States*

RECEIVED ON AUGUST 19, 2012

### CONSPECTUS

A heterogeneous catalyst in industry consists of nanoparticles with variable crystallite sizes, shapes, and compositions. Its catalytic performance (activity, selectivity, and durability) derives from surface chemistry of catalyst nanoparticles during catalysis. However, the surface chemistry of the catalyst particles during catalysis, termed in-situ information, is a “black box” because of the challenges in characterizing the catalysts during catalysis. The lack of such in-situ information about catalysts has limited the understanding of catalytic mechanisms and the development of catalysts with high selectivity and activity.



The challenges in understanding heterogeneous catalysis include measurement of reaction kinetics, identification of reaction intermediates, bridging pressure gap and materials gap. The pressure gap is the difference in surface structure and chemistry between a catalyst during catalysis and under an ultrahigh vacuum (UHV) condition. The materials gap represents the difference between the structural and compositional complexity of industrial catalysts and the well-defined surface of model catalysts of metals or oxides.

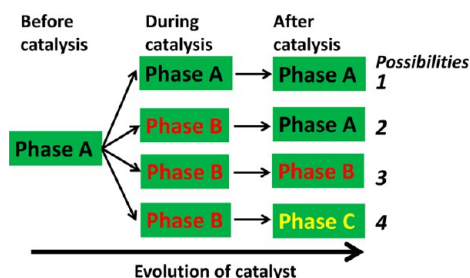
Development of in-situ characterization using electron spectroscopy and electron microscopy in recent decades has made possible studies of surface chemistry and structure of nanocatalysts under reaction conditions or during catalysis at near ambient pressure. In this Account, we review the new chemistries and structures of nanocatalysts during reactions revealed with in-situ analytical techniques. We discuss changes observed during catalysis including the evolution of composition, oxidation state, phase, and geometric structure of the catalyst surface, and the sintering of catalysts. These surface chemistries and structures have allowed researchers to build a correlation between surface chemistry and structure of active nanocatalysts and their corresponding catalytic performances. Such a correlation provides critical insights for understanding catalysis, optimization of existing nanocatalysts, and development of new nanocatalysts with high activity and selectivity.

### 1. Introduction

Heterogeneous catalysis is a chemical process performed at a solid–gas or solid–liquid interface. In most industrial processes of heterogeneous catalysis, reactant gases, typically 760 Torr or higher, flow through a catalyst bed at a high temperature. Crystallites of industrial catalyst particles are at nanoscale, 1–100 nm.<sup>1</sup> Thus, the studies of catalysts are an essential part of nanoscience and nanotechnology, recently termed nanocatalysis. However it is different from the nanosciences focusing on physical properties of nanomaterials such as band gap, electron-transfer, photoexcitation, and absorption, which deal with the static structure

and physical properties of nanocrystals. In these cases, the surface chemistry of nanomaterials is not strongly related to their functions.

As catalytic processes are performed on the surface of nanocatalysts under working conditions, surface chemistry of these materials could experience significant changes when compared to that before and/or after catalysis.<sup>2</sup> Figure 1 schematically presents the potential evolutions of nanocatalysts from an as-synthesized catalyst to the catalyst after reaction. Surface chemistry of a nanocatalyst during catalysis could be similar to those prior to (possibility 1) or after reaction (possibility 3). In these cases, ex-situ studies can provide



**FIGURE 1.** Possible evolution of surface phase of a catalyst before, during and after catalysis.

information of the nanocatalyst during catalysis and aid the understanding of catalytic mechanisms. However, in possibility 2 and 4, surface phase during catalysis is neither the same as that before nor that after catalysis; thus, to understand their catalytic mechanisms it is necessary to obtain surface chemistry of the active phase during catalysis. As fresh surface or subsurface of active catalysts could be oxidized upon exposed to ambient environment, a large number of reactions can be categorized into possibilities 2 and 4 since an active phase, metal or oxide surfaces with oxygen vacancies could be oxidized easily once they are exposed to an ambient environment. Ideally, in any of the four cases in Figure 1, in-situ characterization should be applied to check whether the catalyst experiences change of surface chemistry or not.

This Account mainly discusses the new chemistries of catalysts during reactions revealed with in-situ analytical techniques (mainly environmental electron microscopy), which makes it different from previous reviews focusing on in-situ studies of bimetallic catalysts,<sup>2,3</sup> and introductory review of chemistry and structure of materials in reactive environments.<sup>4</sup> Here we discuss the evolution of composition, oxidation state and phase, and geometric structure of catalyst surface, and sintering of catalysts during catalysis which are topics different from the published reviews.<sup>2-4</sup>

## 2. In-Situ Characterization to Bridge the Gap

The key components in understanding heterogeneous catalysis include the chemistry and structure of a catalyst surface and the formed adsorbates during catalysis. Typically, surface adsorbates can be examined with vibrational spectroscopy. As vibrational spectroscopy is a photon-in-photon-out technique, there is not a technical gap in its applications to catalysis studies. In terms of surface chemistry of a catalyst, X-ray photoelectron spectroscopy (XPS) is one of the major techniques since it can identify oxidation states, chemical compositions, depth-dependent distribution of elements, and electronic states.<sup>5,6</sup> In addition, ambient

pressure XPS (AP-XPS) can provide information of gas phase above a catalyst other than adsorbates and surface of the catalyst. More importantly, the limited inelastic mean free path of photoelectrons in a solid makes it a surface-sensitive analytical technique when soft X-rays (<1500 eV) are used. Since heterogeneous catalysis is performed on the surface of catalysts, this surface-sensitive technique makes it capable of distinguishing surface information from bulk.<sup>7</sup> However, because it is a photon-in-electron-out technique, a shorter mean free path of photoelectrons in an ambient pressure gaseous environment seriously limits the applications of this powerful technique to studies of catalyst surfaces in ambient environment.

Some years after the birth of XPS technique, Siegbahn and co-workers had made efforts in studying sample surfaces under a relatively high pressure.<sup>8-11</sup> Further efforts have been made by a few groups.<sup>12,13</sup> One approach is to use an aperture to separate high pressure environment of catalytic reactants from the vacuum side of the energy analyzer. In 2002, the first synchrotron-based ambient pressure XPS (AP-XPS) was invented.<sup>14</sup> Focusing lenses were used to increase the collection rate for the first time. After this invention, a few other AP-XPS instruments were built.<sup>15</sup> Details of instrumentation can be found in the literature.<sup>16,17</sup> Different from high vacuum XPS, AP-XPS can provide information of the surface of a catalyst, adsorbate, and also the reactant gases above the catalyst.

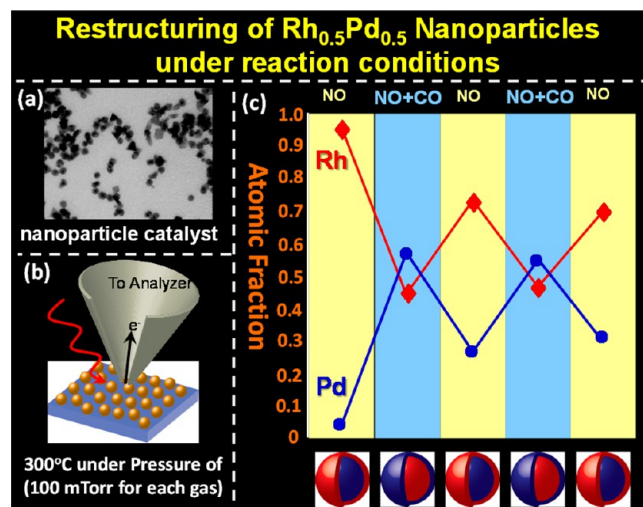
A catalysis event occurs on specific surface sites, which consist of one or several atoms of surface of metal, oxide, or nanocomposited metal-oxide. Information on surface sites of catalysts can be acquired from a scanning tunneling microscope (STM) or other surface-sensitive microscopy technique.<sup>18</sup> In the last three decades, STM has been extensively used in numerous fields such as imaging surface geometric and electronic structures at the atomic level in vacuum and breaking or formation of chemical bonds through manipulation in UHV. Although this technique is not limited to UHV, the reaction conditions (pressure of gas around the surface and temperature of the catalyst) significantly impact its functions and further applications; for instance, a high reaction temperature certainly induces thermal drift of the tip. Thus, for a specific application in visualizing catalysts' surface during catalysis, instrumentation is necessary. One straightforward approach successfully used in early studies of model catalyst surfaces in reactant environment is filling reactant gas into a UHV chamber.<sup>19,20</sup> This approach allows for the study of surface structures at room temperature up to 760 Torr. Recently, a high pressure STM with an integrated reaction cell was built by a few

groups,<sup>21–26</sup> which allows for visualization of surface of a catalyst in reactant gases at a pressure up to 760 Torr or higher. Recent studies showed that subsurface could play important role in catalysis since it could influence electron structure and packing of atoms of the topmost layer of a catalyst.

The rapid development of electron microscopy in the past decade has offered the possibility of identifying the phase and chemical composition of nanocatalysts in gaseous environments or even liquids. The technique is referred to as environmental transmission electron microscopy (E-TEM).<sup>27,28</sup> Other than these techniques, there are several other well-developed techniques for operando studies, which examine structure and composition of the bulk phase of nanocatalysts under reaction conditions or during catalysis, including X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and X-ray diffraction (XRD). Excellent reviews on those techniques have been published in literature.<sup>29,30</sup> XANES, EXAFS, and XRD provide valuable information of catalysts when particles are in size of a few nanometers or smaller. With the development of characterization techniques of nanocatalysts at conditions of ambient pressure or higher, many new chemistries under reaction conditions or during catalysis have been uncovered.

### 3. Evolution of Surface Composition of Nanocatalysts during Reactions

Surface composition of a bimetallic nanocatalyst could be changed upon heating to a high temperature in UHV. In most of these cases, atoms of a metal with a lower surface energy will segregate to the surface; thus, a higher concentration of such a metal in the surface region is expected. However, the evolution of the surface composition during catalysis could be different with respect to the presence of different reactant gases. One example is the reactant-dependent evolution of surface composition driven by interactions between the reactant gas and the bimetallic,  $\text{Rh}_{0.5}\text{Pd}_{0.5}$  nanocatalyst.<sup>31</sup> Depth-profile analysis showed that the as-synthesized nanoparticle has Rh-rich shell and Pd-rich core.<sup>31</sup> However, its composition changed when these bimetallic NPs were exposed to different reactant gases as shown in Figure 2. For example, the atomic fraction of Rh in the surface region (defined to the region from 0.1 to 1.0 nm deep) at 300 °C in nitric oxide or oxygen was ~97% with an error of 5%. However, when carbon monoxide was introduced and a mixture of reactant gases was formed, the surface composition changed to Pd-rich surface with atomic fraction of Pd of ~52%. Clearly, the surface region was restructured largely upon changing the reactant gas.



**FIGURE 2.** Evolution of  $\text{Rh}_{0.5}\text{Pd}_{0.5}$  bimetallic nanocatalysts under different reaction conditions. (a) TEM image of  $\text{Rh}_{0.5}\text{Pd}_{0.5}$  with a size of ~16 nm. (b) Schematic of ambient pressure XPS studies. (c) Evolution of surface composition under different reaction conditions; The models at the bottom illustrate the restructuring of composition in surface region (“shell”) and deep region. Red and blue represent Rh and Pd, respectively. Adapted from ref 31.

The outcome was the migration of Rh atoms to deep region and the segregation of Pd atoms to the surface region. The significant change of surface composition, driven by switching reactant gases, was termed reaction-driven restructuring. Such a restructuring could cycle a few times though the segregated amount decreased progressively, probably due to the formation of carbides or other reactions.

Figure 2 presents the evolution of surface composition of  $\text{Rh}_{0.5}\text{Pd}_{0.5}$  bimetallic nanoparticle in different reactants at Torr pressure range. The evolution of surface composition of  $\text{Rh}_x\text{Pd}_{1-x}$ ,  $\text{Rh}_x\text{Pt}_{1-x}$ , and  $\text{Pd}_x\text{Pt}_{1-x}$  nanoparticles could be determined by two main factors. One is the surface energy of the constituent metals. The other is the adsorption energy of reactant molecules on the metal atoms. When adsorption energies of a molecule on two constituting metals are similar, surface energies of the constituting metals play a major role. In this case, the surface composition is determined by the surface energies. Typically, the surface energy of single crystals can be used to evaluate a trend of surface segregation. However, when the adsorption energies of a reactant on the constituting metals are quite different or the formation energies of surface phases (such as metal oxides) are quite different, the trend of segregation, and thus the surface composition and oxidation state, are mainly determined by the adsorption energies or formation energies of surface compounds. Generally, the constituting element, which has larger adsorption energy or preferentially forms

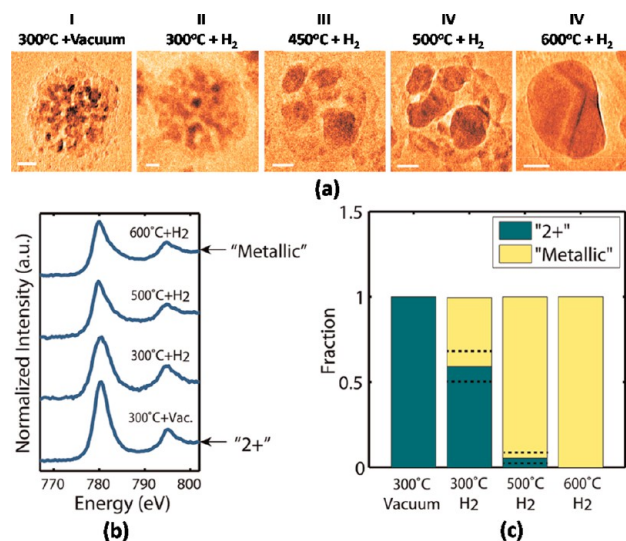


metallic oxide or other compound, will dominate the surface composition, though other effects can reverse the trend.<sup>32</sup>

Change of surface composition was also observed on another type of nanocatalysts. They are nanocomposited metal core (B) and oxide shell ( $\text{AO}_x$ ). In general,  $\text{AO}_x$  shell can form on core of metallic B, leading to a nanocomposited  $\text{B@AO}_x$  catalyst. Although there is a boundary of core of metal B and shell of oxide  $\text{AO}_x$  in the as-synthesized catalyst, the oxide shell could be partially or completely reduced to metallic A by  $\text{H}_2$  of pretreatment or reducing reactant during catalysis to thus form A-B alloy. One excellent example<sup>33</sup> is the formation of a highly active phase of CO oxidation from  $\text{CuO}_x$  nanopatches supported on Au core through reduction in  $\text{H}_2$  with a followed oxidation during catalysis. This as-synthesized  $\text{Au@CuO}_x$  nanocomposited catalyst particles ( $\sim 3$  nm) were synthesized through grafting  $\text{H}_2\text{N}(\text{CH}_2)_3\text{-Si}(\text{OEt})_3$  on silica surface with a followed impregnation and reduction with  $\text{NaBH}_4$ .<sup>33</sup> A calcination in air at 500 °C forms  $\text{CuO}_x$  shell. The as-synthesized catalyst consists of a Au core and a  $\text{CuO}_x$  shell. Atomic fraction of Cu on surface of the as-synthesized catalyst is 100% since the shell is pure  $\text{CuO}_x$ . A pretreatment in  $\text{H}_2$  reduces  $\text{CuO}_x$  to metallic Cu which forms  $\text{Au}_3\text{Cu}$  intermediate, in which the atomic fraction of Cu on surface is 25%. While it is exposed to reactant gases (CO and  $\text{O}_2$ ) an interesting restructuring is observed;  $\text{CuO}_x$  nanopatches are formed on the surface of Au core.<sup>33</sup> During CO oxidation, Cu of  $\text{Au}_3\text{Cu}$  is oxidized, forming discontinuous  $\text{CuO}_x$  nanopatches. The left Au of  $\text{Au}_3\text{Cu}$  forms a metallic Au core. Thus, atomic fraction of Cu in the surface is larger than 25% since  $\text{Au}_3\text{Cu}$  is dealloyed and oxidized to form a ultrathin  $\text{CuO}_x$  nanopatches supported on a relatively larger core of Au. Both exposed  $\text{CuO}_x$  nanopatches and surface of Au core are available sites for a reaction. This restructured surface consists of large fraction of Au atoms at the interface of  $\text{CuO}_x$  nanopatches and Au. In fact, the formed new surface exhibits high activity for CO oxidation at temperature lower than 0 °C. It is attributed to the sites of Au and  $\text{CuO}_x$  located at the interface of Au core and  $\text{CuO}_x$  nanopatches. A similar catalyst, Au–Ag was reported.<sup>34</sup> Its high catalytic activity in CO oxidation is also due to the synergy of Au and  $\text{AgO}_x$ . The promotion role of  $\text{AgO}_x$  in CO oxidation on Au was supported by other work as well.<sup>35</sup>

#### 4. Evolution of Oxidation State and Phase Transformation

Many catalytic processes involve a reducing or oxidizing gas as one of the reactants. The as-synthesized catalysts could be metal, oxide, metal supported on oxide, or oxide



**FIGURE 3.** Evolution of valence state of cobalt catalysts under a series of reaction conditions. (a) E-TEM images of the nanocomposite particle under different reducing environments. (b) Co  $L_{2,3}$  edges of these catalysts, determined from in-situ measurements; (c) fraction of metallic Co at different reaction conditions. Adapted from ref 37. Copyright 2012 American Chemical Society.

supported on metal nanoclusters. In a reactive environment of high temperature, the surface phase, or even both surface and bulk phases, could be reduced or oxidized. In some cases an active phase is formed in-situ.

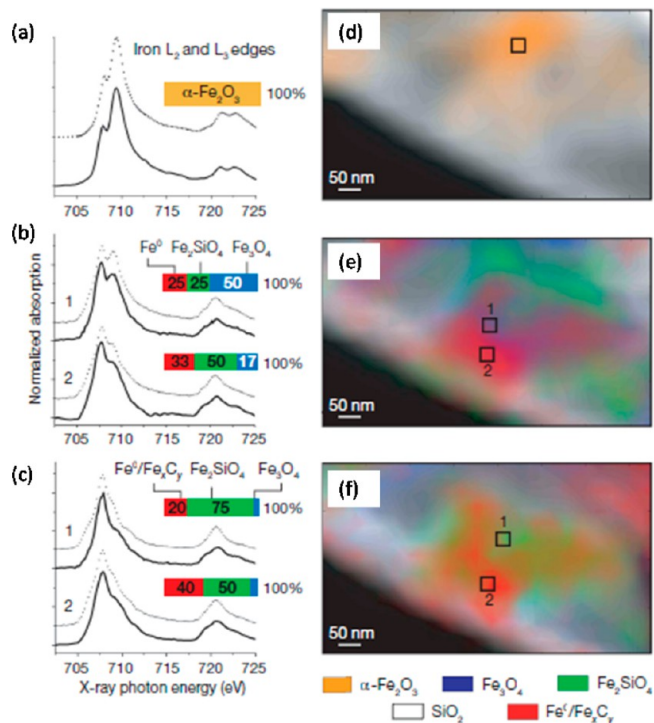
An example is in-situ reduction of cobalt catalyst of Fischer–Tropsch synthesis (FTS). The active cobalt catalyst synthesized through wet chemistry is essentially cobalt oxide.<sup>36</sup> Environmental TEM studies clearly showed the evolution of surface valence state in reducing environment and the associated coarsening at different reaction conditions.<sup>37</sup> The in-situ EELS spectra suggested the progressive reduction of cobalt oxide (Figure 3). Figure 3c clearly shows the fraction of metal portion formed as a function of reduction conditions.

Another example is a Fe catalyst for FTS. The as-synthesized  $\text{Fe}_2\text{O}_3$  catalyst experiences a significant change under pretreatment and during catalysis.<sup>38</sup> In  $\text{CO}+\text{H}_2$ ,  $\text{Fe}_2\text{O}_3$  encountered a progressive phase transition to  $\text{Fe}_2\text{C}_5$ . This phase transition was visualized by X-ray scanning microscopy (Figure 4).  $\text{Fe}_2\text{O}_3$  was first reduced to metallic Fe which, under reaction conditions, dissociates CO and forms iron carbide. The iron carbide is the actual active phase for FTS.<sup>39</sup>

In terms of three-way catalytic converter and high-temperature fuel cells applications, ceria zirconia nanoparticles play a critical role as catalysts due to their ability of switching oxidation states in response to the chemical potential of oxygen. Investigation of redox activity of this material needs

to be done in-situ since partially reduced cerium oxide is unstable at low temperature and/or in any relatively high oxygen partial pressure. In-situ E-TEM analysis

at 480–590 °C in 1.5 Torr of dry H<sub>2</sub> showed that individual ceria zirconia NPs have different reduction activity<sup>40</sup> (EELS insets of Figure 5a and b). Correlation between oxidation state and reduction temperature (Figure 5c) showed that the active particle can change its oxidation state from +4 to +3, along with the increase of working temperature, while the nonactive one had minor change.

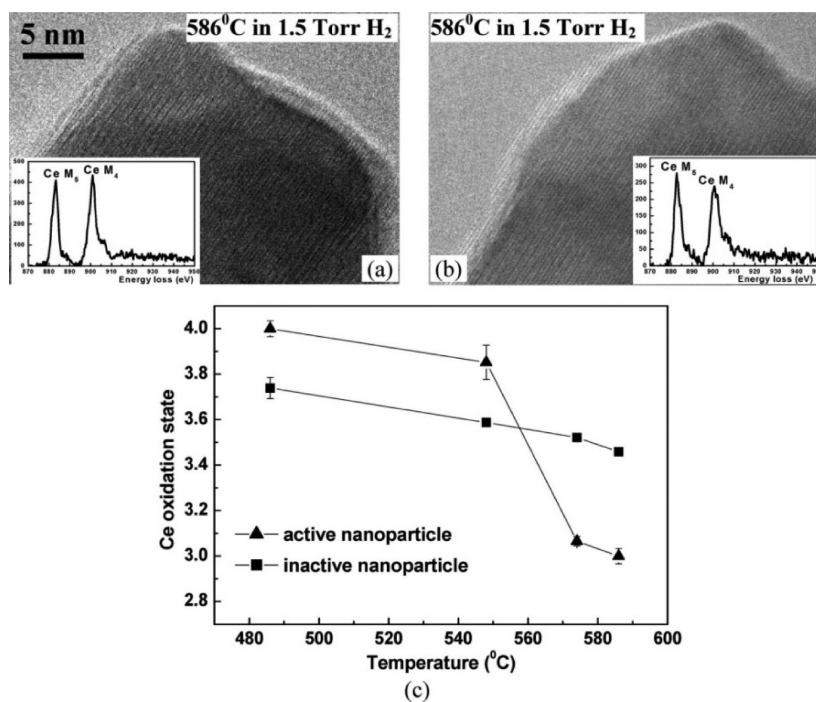


**FIGURE 4.** Represented X-absorption spectroscopy (a–c) of Fe catalysts of Fischer–Tropsch synthesis and chemical contour maps (d–f). Reproduced from ref 38.

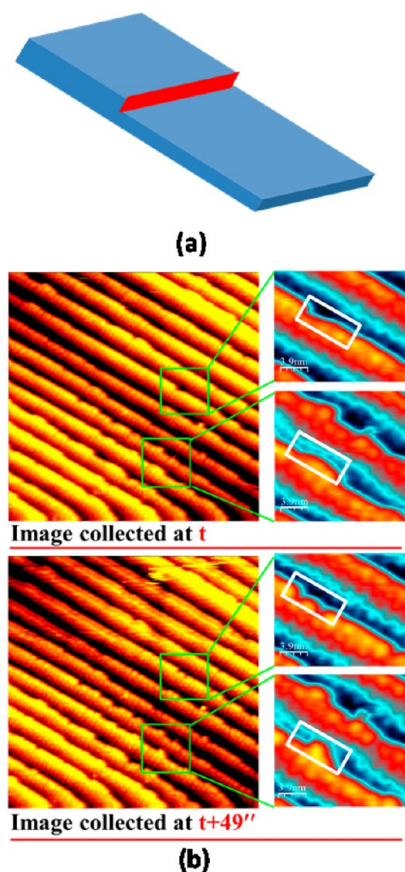
## 5. Geometric Restructuring of Reaction Sites

Oxidation state and phase structure are the average information of nanocatalysts reflecting the surface chemistry and structure over a relatively large scale. Different from some surface chemistry processes such as surface corrosion, a catalysis event is performed on catalytic sites with a specific atomic packing and electronic state on surface of a nanocatalyst. The specific packing of atoms at atomic scale gives appropriate electronic and geometric structures for adsorption of reactant molecules, cleavage of bonds, formation of new bonds by coupling two intermediate species, and a subsequent desorption of product molecules. Characterization of these catalytic sites at nano or atomic scale is crucial in thorough understanding of catalysis. Identification of catalytic sites at atomic level has been most frequently done using STM.<sup>18,41–43</sup>

In most cases, the reactive sites can be atoms at the interface of metal/metal oxide nanoparticles or under-coordinated



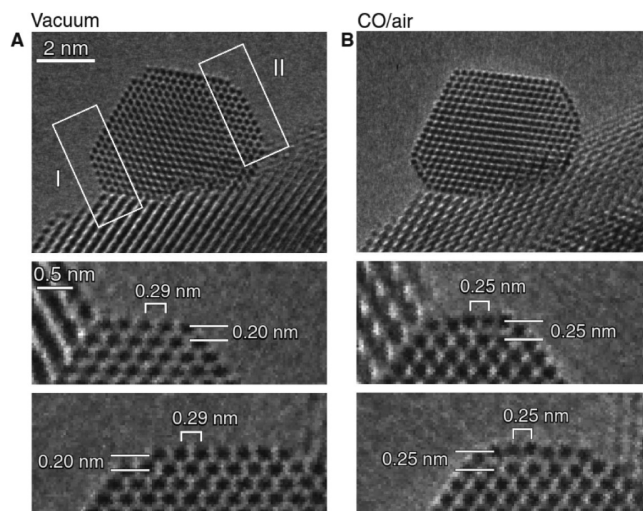
**FIGURE 5.** In-situ E-TEM studies of inactive and active ceria zirconia nanoparticles at 586 °C in 1.5 Torr of H<sub>2</sub>. (a) In-situ TEM of inactive nanoparticles; (b) in-situ TEM of active nanoparticles; (c) evolution of oxidation state of inactive and active nanoparticles. For active nanoparticles, Ce<sup>4+</sup> ions can be reduced to Ce<sup>3+</sup>. Reproduced from ref 40. Copyright 2008 American Chemical Society.



**FIGURE 6.** Restructuring of atoms at step edge of Pt(111) at 10 Torr CO at room temperature. (a) Structural model step edge of Pt(111). (b) STM images of the same surface collected at a time lag of about 49 s (images at  $t$  and  $t + 49$  s). Panel (b) adapted with permission from ref 44. Copyright 2013 American Chemical Society.

atoms on the surface of a heterogeneous catalyst. Typically atoms at step edges of a surface or corners of the crystallite nanocatalyst exhibit high activity in molecular or dissociative adsorption. Due to the low coordination number, they are active in breaking chemical bonds through strong bonding with one or two atoms of a reactant molecule. On the other hand, the under-coordinated environment of these atoms makes them highly mobile and they readily participate in restructuring of the catalyst surface. In some cases, such restructuring creates active sites responsible to the reaction condition.

In-situ studies have demonstrated the evolution of these catalysts at nano or atomic scale. One example is the dynamics restructuring of Pt atoms at the edge of Pt(111) surface. As shown in Figure 6a, atoms at the step edge of a large-scale flat terrace have a coordination number of 7. At room temperature, CO molecules are molecularly adsorbed on Pt atoms. The preferential adsorption site is the Pt atoms along the step edge. Vacuum approach has demonstrated



**FIGURE 7.** E-TEM image of gold NP supported on CeO<sub>2</sub> in (A) vacuum and (B) a reaction environment for CO oxidation (1 vol % CO in air gas mixture at 0.45 mbar at room temperature). Regions I and II indicate two (100) facets. Reproduced from ref 45.

that the adsorption of CO molecules does not change the geometric packing of Pt atoms if there is no gaseous environment around the Pt surface.<sup>18</sup> As the coverage of adsorbates in UHV environment is low, the repulsion between two adjacent CO molecules at a step edge is negligible. However, at a relatively high pressure of CO, the coverage is increased. The crowded packing at the step edge could break step. Figure 6b is a STM image of the step edge of Pt(111) in CO of 10 Torr at room temperature collected with a tungsten tip.<sup>44</sup> Within 49 s, the step edge restructured significantly (Figure 6b) and more kink sites and new nanoclusters were formed. It clearly demonstrated the increased mobility of atoms at the step edge in reactant gases in contrast to that in UHV.

Other than interatomic restructuring in a surface layer, there is also an interplanar restructuring performed during catalysis observed with E-TEM. Interplanar restructuring of Au nanoparticles supported on CeO<sub>2</sub> was observed during CO oxidation using E-TEM.<sup>45</sup> Under vacuum conditions, the interplanar distance along  $\langle 100 \rangle$  direction remained unchanged as shown in Figure 7. The interplanar distance between the topmost and second topmost surface layer in high vacuum is 0.20 nm, which is the same as that in bulk of a gold single crystal. However, introduction of 1 vol % CO in air at 0.45 mbar into the system at room temperature resulted in position shifting of the topmost and second topmost layers (Figure 7b). This is due to a mismatched stacking between the two layers, the topmost layer of Au nanoparticles formed a undulating hexagonal lattice while

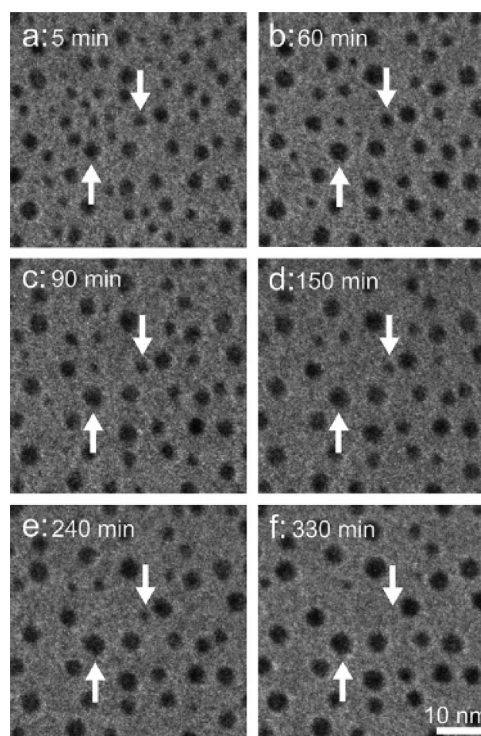


the second topmost layer had a slightly distorted normal square lattice. Evidently, this is a dynamic consequence done by adsorbate–facet interaction at a relatively high pressure of reactants that is only visible during analysis. Although a visualization of surface of nanoparticles at atomic scale is very challenging, these model studies do demonstrate the flexibility of surface atoms and the possibility of restructuring metal atoms under reaction conditions or during catalysis.

## 6. Sintering of Nanocatalysts

As heterogeneous catalysis event is performed on surface of a nanocatalyst, typically noble metals are finely dispersed on a support to increase efficiency on a per atom basis. Small size of nanocatalyst particles and high dispersion make NPs have excess surface energy due to their high-surface area and then become metastable. Given sufficient thermal activation, the NPs will decrease their surface energy by sintering into larger particles. The outcome is typically a decrease in their catalytic performance.<sup>46</sup> Detailed understanding of the sintering mechanism can be difficult due to complex physical and chemical phenomena involved. Two generic sintering mechanisms are often being considered:<sup>47,48</sup> (1) particle migration, in which the nanoparticles diffuse over the support and coalesce with neighboring ones, and (2) atom migration (i.e., Ostwald ripening), in which atoms from one nanoparticle are emitted, diffuse over the support, and reside onto another nanoparticle.

Many in-situ studies regarding sintering mechanisms for industrial nanocatalysts, for example, Pt/SiO<sub>2</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>, have been conducted, which showed different conclusions. For instance, debate in sintering mechanism for Pt/SiO<sub>2</sub> nanoparticles<sup>50–53</sup> was mainly due to the lack of direct and in-situ analysis techniques. Using E-TEM, Helveg et al.<sup>49</sup> unambiguously determined the sintering mechanism of Pt/SiO<sub>2</sub> model catalyst under oxidizing gas environment of 10 mbar synthetic air at 650 °C. Figure 8 shows that the Pt NPs were mobile and their size either increased or decreased. The arrows in each TEM images of Figure 8 indicate examples of growing nanoparticles (marked with up-arrow) and decaying ones (marked with down-arrow), which clearly demonstrates that the sintering process followed the Ostwald ripening mechanism. In-situ studies using E-TEM provided unique mechanistic and kinetic information, for example, temporal evolution of the nanoparticle size, size distribution, and nanoparticle growth rate.<sup>49</sup>



**FIGURE 8.** Time-lapsed in-situ TEM images ( $50 \times 50 \text{ nm}^2$ ) of the Pt/SiO<sub>2</sub> catalyst during exposure to 10 mbar synthetic air at 650 °C. The denoted times are relative to the time at which the temperature reaches 650 °C. Reproduced from ref 49.

## 7. Further Challenges in in-Situ and Operando Studies of Nanocatalysts

Although only some examples of in-situ studies were discussed here due to the limited space, we certainly acknowledged that many other examples were reported in literatures in the last decades. The necessity and significance of in-situ studies of nanocatalysts have been recognized from the increasing number of publications of in-situ studies in catalysis community. From technical point of view, there is no single in-situ technique which could provide enough information for understanding catalysis. The major limit in electron-based techniques such as AP-XPS and E-TEM is the low upper-pressure of operation. Breakthrough in instrumentation toward a higher operational pressure has been highly demanded. In addition, an improvement of in-situ spectroscopy toward a higher spatial resolution is ideal since such a technique could potentially distinguish surface chemistry particle by particle in the future. This is the target of many ongoing efforts in the field of in-situ studies of nanocatalysts.

An ultimate goal of in-situ studies of nanocatalysis is the examination of chemistry (composition, oxide state, and electron structure) of surface, subsurface, or bulk of local

structures of nanocatalysts at nanometer or atomic scale with high temporal resolution during catalysis. To reach this goal, we are facing grand challenges. One is the limit of upper pressure in many in-situ characterizations. Although recent advancement in instrumentation has realized in-situ studies of nanocatalysts at Torr pressure, or near or semi-ambient pressure conditions, these pressure regimes are still lower than the working pressures of catalysts. For example, the upper pressure of current AP-XPS and E-TEM is much lower than 760 Torr. To be able to image catalysts at 760 Torr or higher using E-TEM, one solution is development of an E-TEM sample holder which allows for imaging of a catalyst surface at higher pressure. There have been ongoing efforts of TEM manufacturers including FEI and JEOL. One technical barrier in these efforts is the mechanic and thermal stability of such a sample holder at high temperature in environment of 760 Torr or higher. Another challenge is visualization of catalyst surfaces, model catalysts (flat single crystals, nanoclusters on flat surfaces) at atomic level at a relatively high temperature in ambient pressure of reactants. Therefore, advance of in-situ characterization of catalyst surfaces for achieving high spatial resolution at high temperature is necessary since most of heterogeneous catalysis is performed on catalysts at high temperature in an environment of reactants at ambient pressure or higher. Additional challenge which has been under-presented is the in-situ characterization of nanocatalysts with a high temporal resolution to identify reaction intermediates during catalysis. As ultrafast spectroscopy and fast imaging techniques are critical for tracking chemistry and structure of catalyst surface, subsurface or even bulk, it would be great if a technique/instrument with the functions of in-situ ultrafast spectroscopy and simultaneous fast imaging of a catalyst during catalysis could be available. It could be true in the near future with the advance in TEM technology since high resolution TEM imaging technique with high temporal resolution has been successfully developed in past decade.<sup>54</sup>

*This work is supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy under Grant DE-FG02-12ER1635 (to Tao).*

#### BIOGRAPHICAL INFORMATION

**Shiran Zhang** received his B.S. from University of Science and Technology of China in 2011. Currently, he is a graduate student working on synthesis and in-situ studies of nanocatalysts.

**Luan Nguyen** received his B.S. from Grand Valley State University in 2011. Currently, he is a graduate student working on in-situ studies of surface structure of nanocatalysts.

**Yuan Zhu** received his B.S. from Shanghai University and M.Sc. from Fudan University. He is a graduate student working on synthesis and catalysis of nanomaterials.

**Sihui Zhan** received his Ph.D. from Shandong University. He is currently a visiting scholar from Nankai University.

**Chia-Kuang (Frank) Tsung** received his Ph.D. from UCSB. Currently he is a tenure-track assistant professor at Boston College.

**Franklin (Feng) Tao** received his Ph.D. from Princeton University and worked as a postdoctoral fellow in Lawrence Berkeley National Lab and University of California at Berkeley. Currently he is a tenure-track assistant professor. His research interest is synthesis and in-situ studies of nanocatalysts for catalysis in energy conversion and chemical transformation.

#### FOOTNOTES

\*To whom correspondence should be addressed. E-mail: ftao@nd.edu (Tao) and frank.tsung@bc.edu (Tsung).  
The authors declare no competing financial interest.

#### REFERENCES

- Ertl, G.; Knözinger, H.; Schüth, F.; Weitkamp, J. *Handbook of Heterogeneous Catalysis*; Wiley: Weinheim, 2008.
- Zafeiratos, S.; Piccinin, S.; Teschner, D. Alloys in catalysis: phase separation and surface segregation phenomena in response to the reactive environment. *Catal. Sci. Technol.* **2012**, *2*, 1787–1801.
- Tao, F.; Zhang, S.; Luan, N.; Zhang, X. Action of bimetallic nanocatalysts under reaction conditions and during catalysis: evolution of chemistry from high vacuum conditions to reaction conditions. *Chem. Soc. Rev.* **2012**, *41*, 7980–7993.
- Tao, F.; Salmeron, M. In Situ Studies of Chemistry and Structure of Materials in Reactive Environments. *Science* **2011**, *331*, 171–174.
- Venezia, A. M. X-ray photoelectron spectroscopy (XPS) for catalysts characterization. *Catal. Today* **2003**, *77*, 359–370.
- Deng, X. Y.; Verdager, A.; Herranz, T.; Weis, C.; Bluhm, H.; Salmeron, M. Surface chemistry of Cu in the presence of CO<sub>2</sub> and H<sub>2</sub>O. *Langmuir* **2008**, *24*, 9474–9478.
- Tougaard, S.; Ignatiev, A. Concentration Depth Profiles by XPS - A New Approach. *Surf. Sci.* **1983**, *129*, 355–365.
- Siegbahn, K. *ESCA applied to free molecules*; North-Holland Pub. Co.: Amsterdam, 1970.
- Siegbahn, H.; Siegbahn, K. ESCA applied to liquids. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 319–325.
- Fellner-Feldegg, H.; Siegbahn, H.; Asplund, L.; Kelfve, P.; Siegbahn, K. ESCA applied to liquids IV. A wire system for ESCA measurements on liquids. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *7*, 421–428.
- Siegbahn, H.; Svensson, S.; Lundholm, M. A new method for ESCA studies of liquid-phase samples. *J. Electron Spectrosc. Relat. Phenom.* **1981**, *24*, 205–213.
- Joyner, R. W.; Roberts, M. W.; Yates, K. A "high-pressure" electron spectrometer for surface studies. *Surf. Sci.* **1979**, *87*, 501–509.
- Ruppender, H. J.; Grunze, M.; Kong, C. W.; Wilmers, M. In situ X-ray photoelectron spectroscopy of surfaces at pressures up to 1 mbar. *Surf. Interface Anal.* **1990**, *15*, 245–253.
- Ogletree, D. F.; Bluhm, H.; Lebedev, G.; Fadley, C. S.; Hussain, Z.; Salmeron, M. A differentially pumped electrostatic lens system for photoemission studies in the millibar range. *Rev. Sci. Instrum.* **2002**, *73*, 3872–3877.
- Grass, M. E.; Karlsson, P. G.; Aksoy, F.; Lundqvist, M.; Wannberg, B.; Mun, B. S.; Hussain, Z.; Liu, Z. New ambient pressure photoemission endstation at Advanced Light Source beamline 9.3.2. *Rev. Sci. Instrum.* **2010**, *82*, 053106.
- Salmeron, M.; Schlol, R. Ambient pressure photoelectron spectroscopy: A new tool for surface science and nanotechnology. *Surf. Sci. Rep.* **2008**, *63*, 169–199.
- Knop-Gericke, A.; Kleimenov, E.; Haevecker, M.; Blume, R.; Teschner, D.; Zafeiratos, S.; Schloegl, R.; Bukhtiyarov, V. I.; Kaichev, V. V.; Prosvirin, I. P.; Nizovskii, A. I.; Bluhm, H.; Barinov, A.; Dudin, P.; Kiskinova, M. X-Ray Photoelectron Spectroscopy for Investigation of



- Heterogeneous Catalytic Processes. In *Advances in Catalysis*; Gates, B. C., Knozinger, H., Eds.; 2009; Vol. 52, pp 213–272.
- 18 Tao, F.; Dag, S.; Wang, L.-W.; Liu, Z.; Butcher, D. R.; Bluhm, H.; Salmeron, M.; Somorjai, G. A. Break-Up of Stepped Platinum Catalyst Surfaces by High CO Coverage. *Science* **2010**, *327*, 850–853.
  - 19 McIntyre, B. J.; Salmeron, M.; Somorjai, G. A. A variable pressure/temperature scanning tunneling microscope for surface science and catalysis studies. *Rev. Sci. Instrum.* **1993**, *64*, 687–691.
  - 20 Jensen, J. A.; Rider, K. B.; Chen, Y.; Salmeron, M.; Somorjai, G. A. High pressure, high temperature scanning tunneling microscopy. *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.* **1999**, *17*, 1080–1084.
  - 21 Laegsgaard, E.; Osterlund, L.; Thosttrup, P.; Rasmussen, P. B.; Stensgaard, I.; Besenbacher, F. A high-pressure scanning tunneling microscope. *Rev. Sci. Instrum.* **2001**, *72*, 3537–3542.
  - 22 McIntyre, B. J.; Salmeron, M.; Somorjai, G. A. A Variable Pressure Temperature Scanning Tunneling Microscope for Surface Science and Catalysis Studies. *Rev. Sci. Instrum.* **1993**, *64*, 687–691.
  - 23 Petersen, L.; Schunack, M.; Schaefer, B.; Linderoth, T. R.; Rasmussen, P. B.; Sprunger, P. T.; Laegsgaard, E.; Stensgaard, I.; Besenbacher, F. A fast-scanning, low- and variable-temperature scanning tunneling microscope. *Rev. Sci. Instrum.* **2001**, *72*, 1438–1444.
  - 24 Rasmussen, P. B.; Hendriksen, B. L. M.; Zeijlemaker, H.; Ficke, H. G.; Frenken, J. W. M. The “reactor STM”: A scanning tunneling microscope for investigation of catalytic surfaces at semi-industrial reaction conditions. *Rev. Sci. Instrum.* **1998**, *69*, 3879–3884.
  - 25 Rossler, M.; Geng, P.; Wintterlin, J. A high-pressure scanning tunneling microscope for studying heterogeneous catalysis. *Rev. Sci. Instrum.* **2005**, *76*, 023705.
  - 26 Tao, F.; Tang, D.; Salmeron, M.; Somorjai, G. A. A new scanning tunneling microscope reactor used for high-pressure and high-temperature catalysis studies. *Rev. Sci. Instrum.* **2008**, *79*, 084101.
  - 27 Gai, P. L.; Boyes, E. D.; Helveg, S.; Hansen, P. L.; Giorgio, S.; Henry, C. R. Atomic-resolution environmental transmission electron microscopy for probing gas-solid reactions in heterogeneous catalysis. *MRS Bull.* **2007**, *32*, 1044–1050.
  - 28 Crozier, P. A.; Wang, R.; Sharma, R. In situ environmental TEM studies of dynamic changes in cerium-based oxides nanoparticles during redox processes. *Ultramicroscopy* **2008**, *108*, 1432–1440.
  - 29 Frenkel, A. I. Applications of extended X-ray absorption fine-structure spectroscopy to studies of bimetallic nanoparticle catalysts. *Chem. Soc. Rev.* **2012**, *41*, 8163–8178.
  - 30 Chen, W.; Fan, Z.; Pan, X.; Bao, X. Effect of confinement in carbon nanotubes on the activity of Fischer–Tropsch iron catalyst. *J. Am. Chem. Soc.* **2008**, *130*, 9414–9419.
  - 31 Tao, F.; Grass, M. E.; Zhang, Y. W.; Butcher, D. R.; Renzas, J. R.; Liu, Z.; Chung, J. Y.; Mun, B. S.; Salmeron, M.; Somorjai, G. A. Reaction-Driven Restructuring of Rh–Pd and Pt–Pd Core–Shell Nanoparticles. *Science* **2008**, *322*, 932–934.
  - 32 Andersson, K. J.; Calle-Vallejo, F.; Rossmel, J.; Chorkendorff, L. Adsorption-Driven Surface Segregation of the Less Reactive Alloy Component. *J. Am. Chem. Soc.* **2009**, *131*, 2404–2407.
  - 33 Liu, X.; Wang, A.; Li, L.; Zhang, T.; Mou, C.-Y.; Lee, J.-F. Structural changes of Au–Cu bimetallic catalysts in CO oxidation: In situ XRD, EPR, XANES, and FT-IR characterizations. *J. Catal.* **2011**, *278*, 288–296.
  - 34 Wang, A. Q.; Liu, J. H.; Lin, S. D.; Lin, T. S.; Mou, C. Y. A novel efficient Au–Ag alloy catalyst system: preparation, activity, and characterization. *J. Catal.* **2005**, *233*, 186–197.
  - 35 Zielasek, V.; Juergens, B.; Schulz, C.; Biener, J.; Biener, M. M.; Hamza, A. V.; Baeumer, M. Gold catalysts: Nanoporous gold foams. *Angew. Chem., Int. Ed.* **2006**, *45*, 8241–8244.
  - 36 Xie, X.; Li, Y.; Liu, Z.-Q.; Haruta, M.; Shen, W. Low-temperature oxidation of CO catalysed by Co<sub>3</sub>O<sub>4</sub> nanorods. *Nature* **2009**, *458*, 746–749.
  - 37 Xin, H. L.; Pach, E. A.; Diaz, R. E.; Stach, E. A.; Salmeron, M.; Zheng, H. Revealing Correlation of Valence State with Nanoporous Structure in Cobalt Catalyst Nanoparticles by In Situ Environmental TEM. *ACS Nano* **2012**, *6*, 4241–4247.
  - 38 de Smit, E.; Swart, I.; Creemer, J. F.; Hoveling, G. H.; Gilles, M. K.; Tylliszczak, T.; Kooymann, P. J.; Zandbergen, H. W.; Morin, C.; Weckhuysen, B. M.; de Groot, F. M. Nanoscale chemical imaging of a working catalyst by scanning transmission X-ray microscopy. *Nature* **2008**, *456*, 222–225.
  - 39 de Smit, E.; Weckhuysen, B. M. The renaissance of iron-based Fischer–Tropsch synthesis: on the multifaceted catalyst deactivation behaviour. *Chem. Soc. Rev.* **2008**, *37*, 2758–2781.
  - 40 Wang, R.; Crozier, P. A.; Sharma, R.; Adams, J. B. Measuring the redox activity of individual catalytic nanoparticles in cerium-based oxides. *Nano Lett.* **2008**, *8*, 962–967.
  - 41 Merte, L. R.; Peng, G.; Bechstein, R.; Rieboldt, F.; Farberow, C. A.; Grabow, L. C.; Kudernatsch, W.; Wendt, S.; Laegsgaard, E.; Mavrikakis, M.; Besenbacher, F. Water-Mediated Proton Hopping on an Iron Oxide Surface. *Science* **2012**, *336*, 889–893.
  - 42 Besenbacher, F.; Chorkendorff, I.; Clausen, B. S.; Hammer, B.; Molenbroek, A. M.; Norskov, J. K.; Stensgaard, I. Design of a surface alloy catalyst for steam reforming. *Science* **1998**, *279*, 1913–1915.
  - 43 Mitsui, T.; Rose, M. K.; Fomin, E.; Ogletree, D. F.; Salmeron, M. Dissociative hydrogen adsorption on palladium requires aggregates of three or more vacancies. *Nature* **2003**, *422*, 705–707.
  - 44 Luan, N.; Cheng, F.; Zhang, S.; Tao, F. Visualization of Surfaces of Pt and Ni Model Catalysts in Reactive Environments Using Ambient Pressure High Temperature Scanning Tunneling Microscopy and Understanding the Restructurings of Surfaces of Model Metal Catalysts under Reaction Conditions at Near Ambient Pressure. *J. Phys. Chem. C* **2013**, *117*, 971–977.
  - 45 Yoshida, H.; Kuwauchi, Y.; Jinschek, J. R.; Sun, K.; Tanaka, S.; Kohyama, M.; Shimada, S.; Haruta, M.; Takeda, S. Visualizing Gas Molecules Interacting with Supported Nanoparticulate Catalysts at Reaction Conditions. *Science* **2012**, *335*, 317–319.
  - 46 Bartholomew, C. H. Mechanisms of catalyst deactivation. *Appl. Catal., A* **2001**, *212*, 17–60.
  - 47 Wynblatt, P.; Gjostein, N. A. Supported metal crystallites. *Prog. Solid State Chem.* **1975**, *9*, 21–58.
  - 48 Wanke, S. E.; Flynn, P. C. The Sintering of Supported Metal Catalysts. *Catal. Rev.* **1975**, *12*, 93–135.
  - 49 Simonsen, S. B.; Chorkendorff, I.; Dahl, S.; Skoglundh, M.; Sehested, J.; Helveg, S. Ostwald ripening in a Pt/SiO<sub>2</sub> model catalyst studied by in situ TEM. *J. Catal.* **2011**, *281*, 147–155.
  - 50 Doring, T. A.; Lynch, B. W. J.; Moss, R. L. The structure and activity of supported metal catalysts: V. Variables in the preparation of platinum/silica catalysts. *J. Catal.* **1971**, *20*, 190–201.
  - 51 Doring, T. A.; Moss, R. L. The structure and activity of supported metal catalysts: I. Crystallite size and specific activity for benzene hydrogenation of platinum/silica catalysts. *J. Catal.* **1966**, *5*, 111–115.
  - 52 Lee, T. J.; Kim, Y. G. Redispersion of supported platinum catalysts. *J. Catal.* **1984**, *90*, 279–291.
  - 53 Zou, W.; Gonzalez, R. D. Stabilization and sintering of porous Pt/SiO<sub>2</sub>: a new approach. *Appl. Catal., A* **1993**, *102*, 181–200.
  - 54 Paik, D. H.; Lee, I. R.; Yang, D. S.; Baskin, J. S.; Zewail, A. H. Electrons in finite-sized water cavities: Hydration dynamics observed in real time. *Science* **2004**, *306*, 672–675.