FOCUS ARTICLE

ChemComm
www.rsc.org/chemcomm

Catalysis and nanoscience

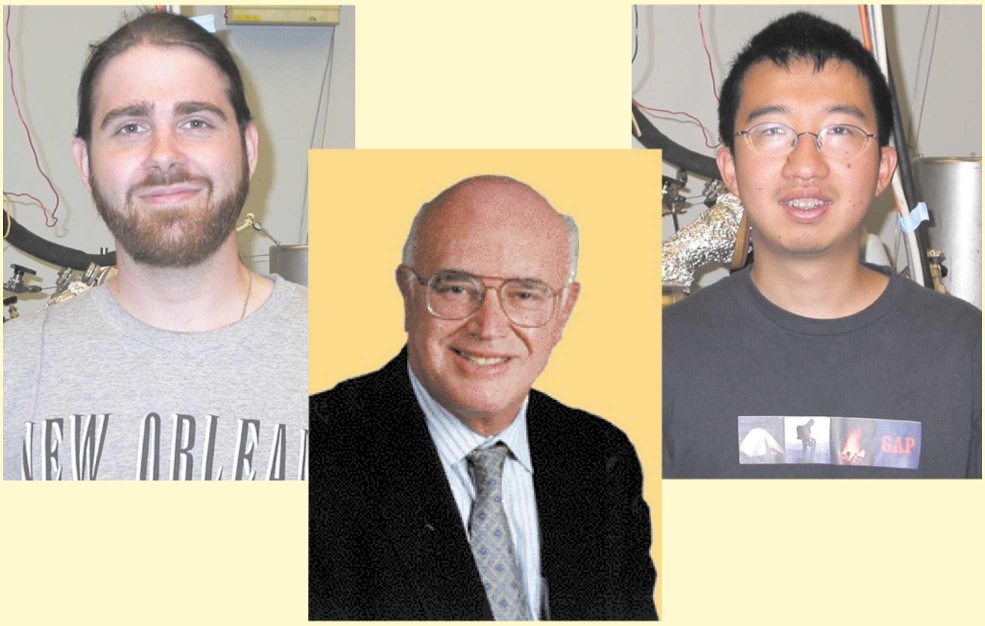
Jeff Grunes,[ab] **Ji Zhu**[ab] **and Gabor A. Somorjai***[ab]

[a]*Department of Chemistry, University of California, Berkeley CA 94720, USA*
[b]*Materials Sciences and Chemistry Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720, USA*

The development of synthetic catalysts is inspired by nature's use of enzymes to achieve high reaction rates and 100% selectivity. These natural catalysts often contain inorganic nanoclusters at the active site, and it is an understanding of the activity and selectivity of these nanoclusters and their interaction with the surrounding protein, which can aid in the design of synthetic catalysts. Since natural and synthetic catalysts are composed of these nanoclusters, the fields of catalysis and nanoscience are inextricably linked.

Catalysis: the central field of nanoscience and nanotechnology

There are two types of catalysts that carry out chemical reactions with high rates and selectivity.[1] Enzymes are nature's catalysts, and many of them are composed of inorganic nanoclusters surrounded by high-molecular-weight proteins. These catalysts help the human body to function and are responsible for the growth of plants. They usually operate at room temperature and in aqueous solution. Synthetic catalysts, either heterogeneous or homogeneous, are often metal nanoclusters that are used in the chemical technologies to carry out reactions with high turnover and selectivity. The



Jeff Grunes (LEFT) received his B.S. in chemistry from Trinity University in San Antonio, Texas, in May 2000. He joined Professor Gabor Somorjai's group at the University of California, Berkeley, and Lawrence Berkeley National Laboratory in August 2000. Jeff has been under Somorjai's supervision, working toward his Ph.D. in physical chemistry in the field of surface science. He has been designing nanofabricated model catalysts and performing reaction studies on these systems.

Ji Zhu (RIGHT) received his B.S. in physical chemistry from the University of Science and Technology of China in 1997. He worked under Professor Gabor Somorjai's supervision from 1998 to 2003 at University of California, Berkeley, earning his Ph.D. in chemistry for his work on surface science and nanofabricated model catalysts. Now he works for Lam Research in Fremont, California.

Gabor Somorjai (CENTRE) received his Ph.D. in chemistry from the University of California, Berkeley, in 1960. He later joined the faculty at University of California, Berkeley, and became a Faculty Senior Scientist at Lawrence Berkeley National Laboratory. Somorjai has implemented a program to build the fundamental molecular basis for the surface science of heterogeneous catalysis. His pioneering work has afforded him such honors as the National Medal of Science, the Linus Pauling Medal and the Wolf Prize in Chemistry.

DOI: 10.1039/b305719b

heterogeneous systems have high catalyst surface area and they frequently operate at high temperatures in the 400–1000 K range. The reactants and products flow by the catalyst interface in the gas phase, if possible, to facilitate high reaction rates and removal of the product molecules from the catalyst bed. Both enzyme and synthetic catalysts are usually nanoclusters in size and thus the fields of catalysis science and technologies are also nanoscience and nanotechnologies. The evolution of the field of catalysis is strongly coupled to the development of nanoscience and nanotechnology at the present. Fig. 1 shows schematically the nanoscale size of catalyst systems. Enzyme catalyst active sites, which are inorganic nanoclusters containing iron, carry out important oxidation and reduction chemistry. Synthetic platinum catalysts, made of platinum nanoclusters dispersed on high surface area γ-alumina, are used for carrying out so-called ‘reforming’ reactions that convert straight chain alkanes, such as *n*-hexane or *n*-heptane, to aromatic molecules or branched isomers of high octane number.

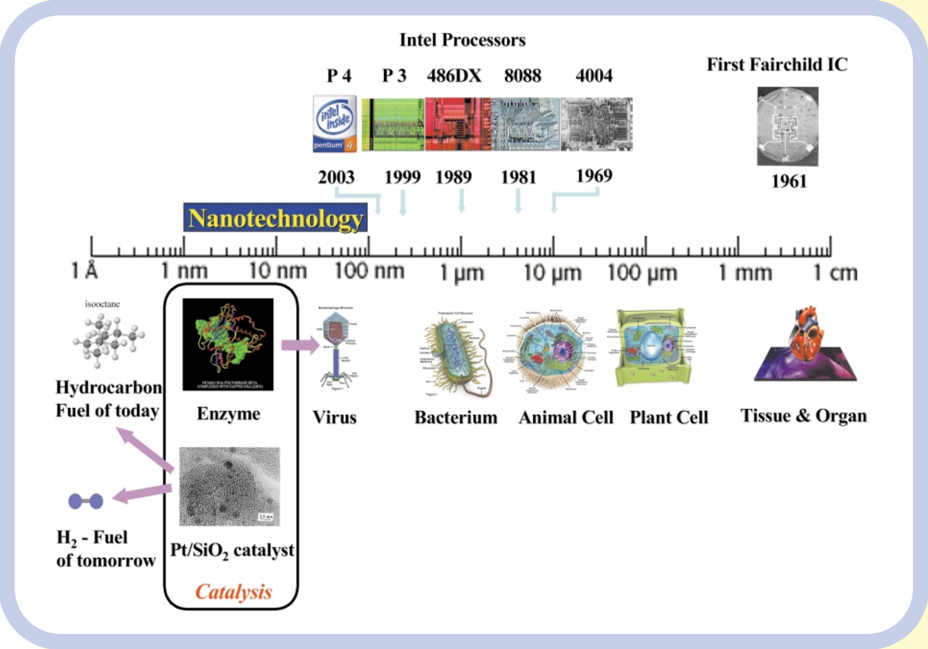


Fig. 1 Catalysts and the nanometer regime.

There are surface technologies for which reduction in size of the active device makes it perform better. Such a device is the microprocessor, for example, where the size reduction of its transistor components increases its speed of operation. The magnetic disc drive is another surface device that benefits from reduction of the recording head-magnetic film (where information is stored) distance that increases the magnetic storage density. These surface technologies are reaching the nanometer dimensions (Fig. 1), and scientific and technological challenges encountered during their fabrication and characterization fuel intensive research in nanosciences. It should be noted and emphasized that both catalysts and surface technologies require a focus on nanoscience for their fabrication and characterization in order to optimize their functioning.

Catalysis in the 20th Century focused primarily on activity, increasing turnover rates to produce more molecules/unit area/unit time.[2] Selectivity was of lesser concern because the disposal of undesirable byproducts as waste was not costly. This has all changed in the 21st Century, because waste disposal is now expensive. As a result, the focus of catalysis science at present is to achieve 100% selectivity in all catalyst-based chemical processes. This is often called green chemistry. The high cost of waste management as well as the ecological impacts of unwanted byproducts have made selectivity the prime concern in designing catalysts, even at the expense of activity.

The known molecular ingredients of catalytic activity and selectivity

Our knowledge of the molecular ingredients of selectivity is poor compared to our understanding of the causes of activity. There are only two multi-path catalytic reactions studied by catalysis science using the surface science approach to explore selectivity. These are CO hydrogenation[3] and the conversion of *n*-hexane or *n*-heptane to branched isomers, aromatics and other products (reforming).[4] There are six important identifiable features that influence both catalyst activity and selectivity. These are metal surface structure, bonding modifier additives, mobility of the metal clusters to restructure as well as the mobility of adsorbates on these clusters, selective site blocking, bifunctional catalysis, and oxide-metal interface sites. Below, we shall give examples of how these catalyst ingredients work to produce improved reactivity and selectivity.

Metal surface structure

The metal surface structure is important in many ways. Hydrogen deuterium exchange,[5] which probes hydrogen dissociation, occurs with unit reaction probability at atomic steps on transition metal surfaces, while on flat, defect-free metal surfaces, the reaction probability is low. In ammonia synthesis,[6] more open surface structures of iron are more active to dissociate di-nitrogen, which is the rate-determining step in producing ammonia by hydrogenation. The two surfaces that are most active are Fe(111) and Fe(211); they both share the presence of C_7 sites, which are thought to be responsible for dissociating di-nitrogen with near zero activation energy.

Bonding modifier additives

By adding a small amount of potassium to iron,[7] the turnover rate for producing ammonia from nitrogen and hydrogen could be increased by 30-fold. The reason for this is that potassium is an electron donor, as is ammonia, which is the product of this catalytic reaction. The presence of potassium weakens the ammonia bonding to the surface; its heat of adsorption to iron is reduced by 2.5 kcal mol^{-1}. Thus, due to this repulsive donor–donor interaction, ammonia’s residence time is shorter on the surface, and therefore it does not inhibit the turnover.

Mobility

During ethylene hydrogenation,[8] the adsorbate-covered Rh(111) surface is disordered as shown by high-pressure scanning tunneling microscopy.[9] Upon poisoning this reaction with carbon monoxide, ordered structures form and the reaction stops. This clearly indicates that poisoning a catalyst surface stops the mobility of adsorbates; this mobility is a key component of catalytic activity. The active platinum surface is covered with strongly adsorbed ethylidyne molecules that restructure the metal surface around the bonding sites.[10] While these adsorbates do not turn over, their role is to prepare the surface for catalytic hydrogenation. Weakly adsorbed, π-bonded ethylene that occupy the remaining metal sites that are not occupied by ethylidyne, hydrogenate rapidly and is the reaction intermediate responsible for turnover.[11]

Selective site blocking

The pore structures of zeolites can be used to inhibit access of larger molecules to the active sites inside the micropores by restricting the pore size of high surface area porous catalysts.[12] By decreasing the pore size, smaller molecules can enter and undergo chemical change, while the bigger molecules cannot. This way, excellent product selectivity can be obtained, such as using zeolites as acid–base catalysts. Blocking undesirable sites, such as kink sites on a metal surface that dissociate carbon–carbon bonds,[13] can modify catalytic selectivity by eliminating an unwanted chemical reaction.

Bifunctional catalysis

Bifunctional catalysis means that sequential or parallel catalytic reactions can occur on more than one type of sites on complex surfaces.[14] Often, a transition metal site is used to dissociate hydrogen and oxygen, but organic rearrangement reactions may occur on oxide surfaces that provide acid–base catalytic sites for isomerization, alkylation, and dehydrocyclization.[15]

Oxide-metal interface sites

Oxide–metal interface sites are often thought to be important in catalysis.[16] This can be shown by placing nickel on various oxide supports. The oxide supports cannot carry out CO hydrogenation reactions;[17] however, when nickel is placed on both oxide supports, the activity and selectivity change dramatically, depending on the type of oxide used.

Fabrication of high-technology catalysts

In order to obtain high selectivity toward the ultimate goal of 100% selectivity, which is a road map for obtaining selective and green catalysts for chemical processes, one has to assert molecular control over the size, location, structure, and promoters of the catalysts. We are attempting to do this by fabricating 2-dimensional and 3-dimensional catalysts.

2-Dimensional and 3-dimensional catalyst fabrication

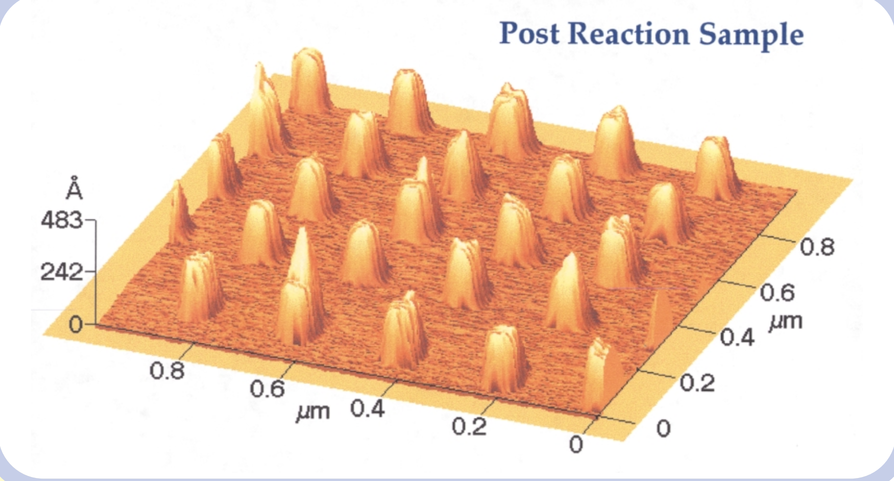


Fig. 2 AFM image of 50 nm Pt nanoparticles with 200 nm spacing on SiO_2, fabricated by electron beam lithography.

Using electron beam lithography,[18] one can obtain nanoparticles of platinum in the size range of 5–50 nm. An atomic force microscope picture of such a structure is shown in Fig. 2. Using electron microscopy, both in the back reflection and in the transmission modes, one can image the nanoparticle array and the structure of each nanoparticle. It was found that upon heating these nanoparticles either in vacuum or in hydrogen or oxygen, they restructured to form highly perfect single crystals. Methods like this allow us to prepare 10^9 nanoparticles in about a day. This amounts to a surface area of 1 mm^2, which is quite small for studies of reaction selectivity. We need about 10^{11} nanoparticles, which would provide a cm^2 surface area, which is adequate to study, for example, reforming reactions or CO hydrogenation reactions. However, that would take 100 days to produce by electron beam lithography. As a result, we have turned to photolithography. A new process called size reduction lithography[19] has been developed in Berkeley permitting us, by selective etching, to reduce the size from 600-nm photolithographically-prepared features down to 7-nm size features. The scheme of this process is shown in Figs. 3 and 4. Fig. 3 shows the overall scheme, while in Fig. 4, the steps that lead to a 50% reduction in size through the first cycle of size reduction lithography is shown. Repetition of such a cycle several times permits us to reach 7 nm in size. Once such a nanowire or nanodot mold

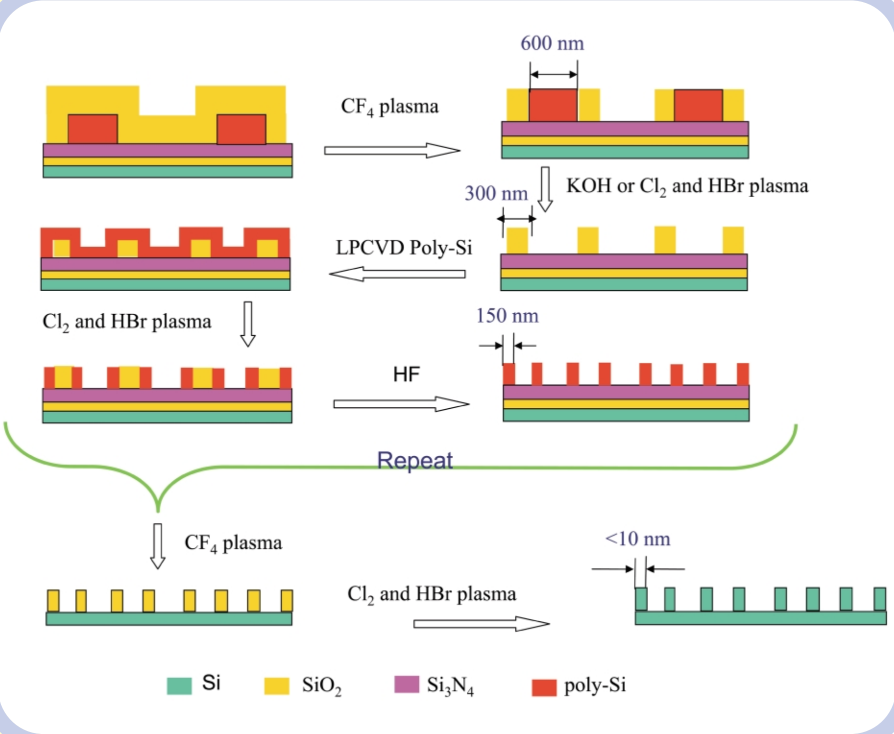


Fig. 3 Scheme for multiple size reduction lithography.

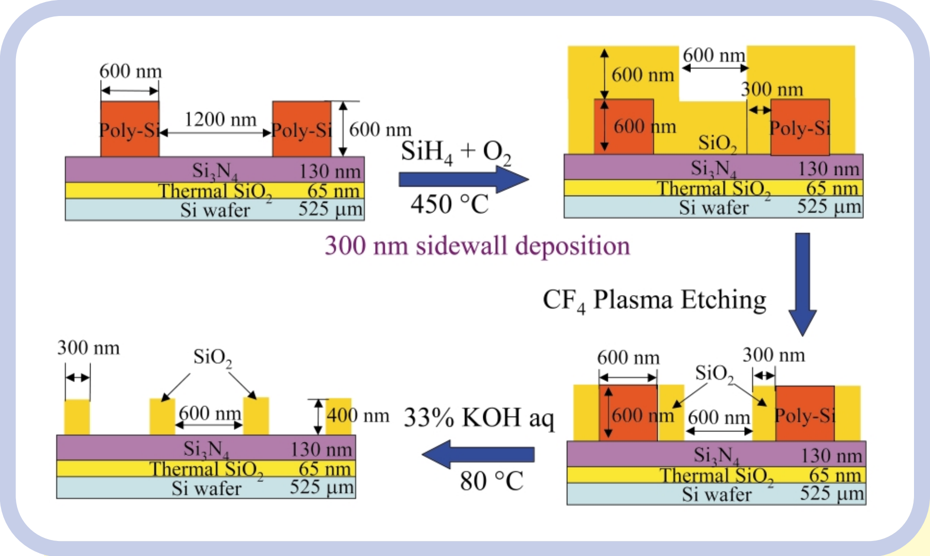


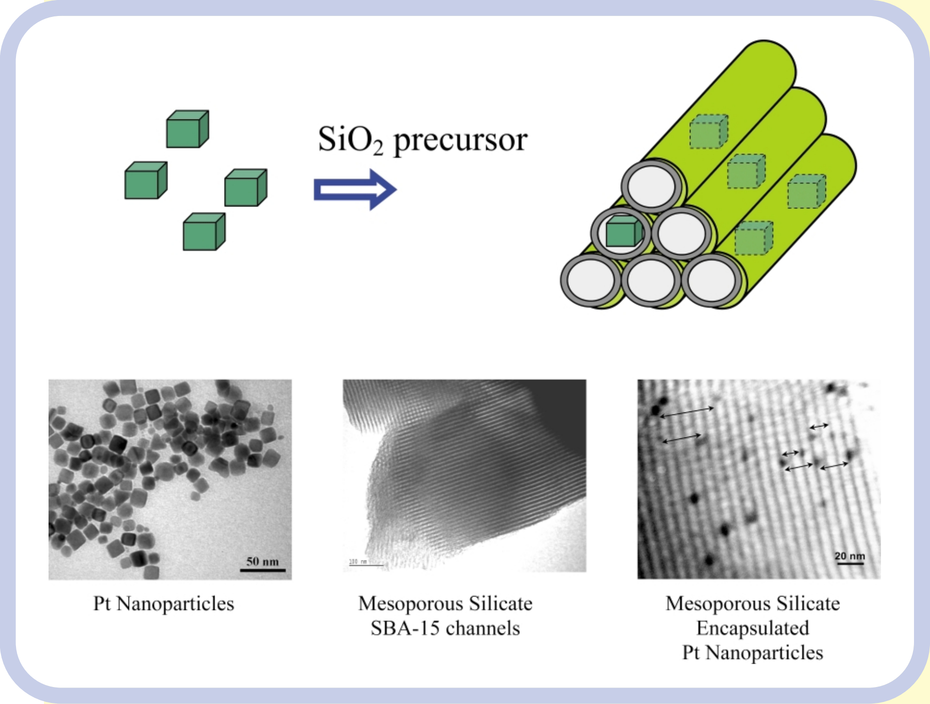
Fig. 4 Focus on the steps of size reduction lithography that results in a 50% reduction in feature size.

has been produced, we use polymer imprinting technology (nanoimprint lithography) to press the silicon nanowires or nanodots into PMMA at elevated temperatures under pressure to produce an image, which upon plasma etching and metal deposition, leads to the formation of transition metal catalyst nanowires or nanodots. This way we can prepare, on a 4-in silicon wafer, a 1-cm^2 surface area nanocatalyst assembly, which amounts to 10^{11} nanowires or nanodots.

If we are to aim for higher catalyst surface area for technological applications of 1 m^2 or higher, it will require the production of 10^{15} nanoparticles or greater in number. This can only be obtained in 3-dimensional structures. Fig. 5 shows our approach.[20] Using a sol-gel technique, we produce nanoparticles of equal size and structure that are capped by polymers. This fabrication is carried out in solution. In the same solution, we then place precursor molecules to form silicates, which, under proper conditions, produce mesoporous silicates that encapsulate the nanoparticles in the mesopores as they form. This way, we can place large concentrations of transition metal nanoparticles inside mesoporous solids to achieve high loading as well as precise size and surface structure control. These approaches are aimed toward producing nanoparticles for very high selectivity catalytic reactions.

It should be noted that enzymes exhibit 100% selectivity in important catalytic reactions, and these enzymes operate at room temperature and in aqueous solutions. Future studies will correlate the chemistry and mechanism of enzyme catalysis with those of synthetic catalysts under the same conditions at room temperature and in aqueous solutions. Such correlated studies are promising to teach us how nature prepares highly selective nanocluster catalysts, and therefore how to synthesize and use them in chemical technology.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.



Pt Nanoparticles

Mesoporous Silicate
SBA-15 channels

Mesoporous Silicate
Encapsulated
Pt Nanoparticles

Fig. 5 Pt nanoparticles encapsulated in mesoporous silicate.

Notes and references

1 *Catal. Lett.*, 2001, **76**, 111–124.
2 G. A. Somorjai and K. McCrea, *Appl. Catal. A-Gen.*, 2001, **222**, 3–18.
3 Y. Borodko and G. A. Somorjai, *Appl. Catal. A-Gen.*, 1999, **186**, 355–362.
4 A. L. D. Ramos, S. H. Kim, P. L. Chen, J. H. Song and G. A. Somorjai, *Catal. Lett.*, 2000, **66**, 5–11.
5 S. L. Bernasek and G. A. Somorjai, *J. Chem. Phys.*, 1975, **62**, 3149–3161.
6 N. D. Spencer, R. C. Schoonmaker and G. A. Somorjai, *J. Catal.*, 1982, **74**, 129–135.
7 D. R. Strongin and G. A. Somorjai, *J. Catal.*, 1988, **109**, 51–60.
8 P. S. Cremer and G. A. Somorjai, *J. Chem. Soc.-Far. Trans.*, 1995, **91**, 3671–3677.
9 K. S. Hwang, M. Yang, J. Zhu, J. Grunes and G. A. Somorjai, *J. Mol. Catal. A* (in press).
10 U. Starke, A. Barbieri, N. Materer, M. A. Van Hove and G. A. Somorjai, *Surf. Sci.*, 1993, **286**, 1–14.
11 P. S. Cremer, X. C. Su, Y. R. Shen and G. A. Somorjai, *J. Am. Chem. Soc.*, 1996, **118**, 2942–2949.
12 V. J. Frilette, P. B. Weisz and R. L. Golden, *J. Catal.*, 1962, **1**, 301–306.
13 F. Zaera and G. A. Somorjai, *Langmuir*, 1986, **2**, 686–688.
14 C. R. Vera, C. L. Pieck, K. Shimizu, J. C. Yori and J. M. Parera, *Appl. Catal. A-Gen.*, 2002, **232**, 169–180.
15 K. Tanabe and W. F. Holderich, *Appl. Catal. A-Gen.*, 1999, **181**, 399–434.
16 A. Boffa, C. Lin, A. T. Bell and G. A. Somorjai, *J. Catal.*, 1994, **149**, 149–158.
17 C. H. Bartholomew, R. B. Pannell and J. L. Butler, *J. Catal.*, 1980, **65**, 335–347.
18 J. Grunes, J. Zhu, E. A. Anderson and G. A. Somorjai, *J. Phys. Chem. B*, 2002, **106**, 11463–11468.
19 Y. K. Choi, J. Zhu, J. Grunes, J. Bokor and G. A. Somorjai, *J. Phys. Chem. B*, 2003, **107**, 3340–3343.
20 Z. Konya, V. F. Puntes, I. Kiricsi, J. Zhu, P. Alivisatos and G. A. Somorjai, *Catal. Lett.*, 2002, **81**, 137–140.