Bridging the Gap between Surface Science and Industrial Catalysis

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ABSTRACT Understanding the structure–activity relationships of catalytic solids has always been hampered by the complexity and nonuniform structures of catalyst particles. Materials based on well-defined colloidal metal particles are ideal model solids to investigate such structure–activity relationships. A new paper by Tsang et al. in this issue indicates that highly selective α,β-unsaturated aldehyde hydrogenation Pt-based catalysts can be obtained following the decoration of Pt nanocrystals with a second metal. The effects of the particle size, substrate shape, and electronic modifications were related to the sample activity. The possibility of depositing these tailor-made colloidal particles onto conventional supports opens exciting new routes toward rational catalyst design and ultraselective catalytic processes.

The enormous impact of heterogeneous catalysis on the quality of our daily life is often underestimated. Transportation fuels, plastics and fibers, fertilizers, pollution control systems, food processing, and fragrances are all classical examples of products or processes in which heterogeneous catalysis plays a role in reducing manufacturing or operation costs and limits waste production. The understanding of the structure–activity relationship of catalytic materials has always been complicated by the complexity and nonuniform structure of catalyst particles, thereby hampering catalyst development. Surface science techniques and the investigation of single-crystal surfaces have been crucial in unraveling many aspects of reaction mechanisms, and the 2007 Nobel Prize awarded to Gerhard Ertl was an acknowledgment of these outstanding achievements.[1] However, industrial catalysts are only remotely related to the perfect surfaces traditionally studied by surface science techniques. Typical commercial materials consist largely of a mixture of phases that can differ in stoichiometry, bulk and surface structure, particle shape and size, defects, impurities, and interactions with a supporting substrate (to different extents), which can induce structural and electronic modifications to the active phase. Usually, the support itself also presents a complex nonhomogeneous surface.

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Nanoparticles as Model Catalytic Systems. The study of model well-defined metal nanoparticles has highlighted important features of heterogeneous catalytic reactions and has been a major step toward understanding industrial catalysts.[2,3] For example, Au-based materials were shown to exhibit markedly different catalytic properties for the oxidation of CO with O_2 depending on the size of Au nanoclusters supported on a single-crystal TiO_2(110) surface. The critical size for the Au nanoclusters was ~3.5 nm diameter, under which high catalytic activity was observed.[4] Lambert and co-workers recently reported the preparation of Au nanoparticles using various synthetic techniques and deposition on a range of inert supports for styrene oxidation with molecular oxygen, for which the critical size for the Au particles was ~2 nm.[5]

Somorjai and co-workers investigated the structure–activity relationship of ~12 nm Pt particles supported on silicon wafers and stabilized with tetradecyltrimethylammonium bromide (TTAB), an emulsifier acting as a stabilizing agent.[6] The Pt nanocrystals exhibited mostly either cuboidal or cuboctahedral shapes; the cubic particles displayed only Pt(100) planes at the surface, while both Pt(100) and Pt(111) planes were present in the case of cuboctahedral crystals (Figure 1). The samples were tested for a structure-sensitive reaction, benzene hydrogenation. Only cyclohexane was observed in the case of the cubic particles, while both cyclohexane and cyclohexene were detected in the case of the cuboctahedral crystals. The intrinsic activity (that is,

See the accompanying Article by Tsang *et al.* on p 2547.

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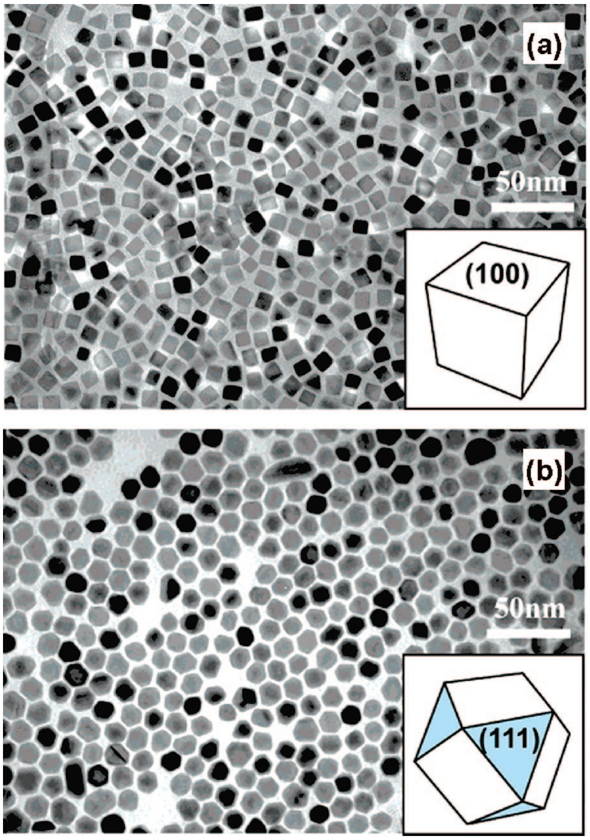

Figure 1. TEM images of TTAB-stabilized particles of platinum with (a) mostly cubic shape (average size: 12.3 ± 1.4 nm) and (b) mostly cuboctahedral shape (average size: 13.5 ± 1.5 nm). Reprinted from ref 6. Copyright 2007 American Chemical Society.

the rate normalized to the number of surface atoms) observed was also different from that calculated from the combination of the activity of Pt(100) and Pt(111) surfaces determined over single-crystals. The Pt atoms at the surface of the nanoparticles exhibited 3-fold higher activity as compared to the Pt atoms present over the corresponding single-crystal surface. These results stress that significant differences can be expected between the activity measured over single-crystal surfaces and that obtained over metal nanoparticles, albeit as large as 12 nm.

Co-Decorated Pt Nanocrystals for Selective Hydrogenation. In an article published in this issue, Tsang *et al.* describe the preparation of nonsupported Pt particles made *via* a colloid technique with various sizes ranging from 24 nm down to 2.8 nm, each sample presenting a narrow size distribution, enabling thorough investigation of any potential size-activity relationship.[7] The 2.8 nm diameter particles correspond to a metal dispersion of ~35%, meaning that about a third of the Pt atoms are located at the surface of the particles. Similar or even higher dispersion is usually sought for commercial catalysts, for obvious activity *versus* material cost reasons. The selective hydrogenation of α,β-unsaturated aldehydes was used as a model reaction, in which the preferential hydrogenation of the carbonyl function to yield an unsaturated alcohol was targeted, while the hydrogenation of the $C{=}C$ would be prevented. The larger particles exhibited the highest selectivity to the unsaturated alcohol, which seemed to level off at ~85% with increasing particle diameter. In contrast, a selectivity lower than 50% was measured for all samples with particle diameter lower than 5 nm.

Tsang *et al.*[7] decorated 4.8 nm-large Pt nanoparticles (typical metal dispersion *ca.* 20%) with cobalt directly in the colloidal suspension used to prepare the metal particles, using cobalt acetyl acetonate as cobalt precursor.[7] This technique is likely to lead to a homogeneous distribution of Co, as opposed to traditional methods, such as incipient wetness impregnation. Interestingly, the authors showed that the Co precursor decomposition was actually catalyzed by the platinum and that the Co uptake was limited, possibly only to Pt sites with a low coordination number. The Co decoration led to an outstanding and unprecedented increase of the selectivity to the unsaturated alcohol, which was above 99% for some of the Co−Pt samples. It is also interesting to note that the Co decoration had essentially no effect on the catalytic activity of Pt particles with diameters larger than 15 nm.

Tsang *et al.*[7] carried out IR studies using carbon monoxide as a probe molecule to cast light on the nature of the Pt sites present in the parent and Co-decorated samples.[7] Unusual Pt-multicarbonyl species were observed in the case of the parent material, along with more common linear and bridged carbonyl species. This observation was probably related to a high concentration of low-coordination Pt atoms forming defective sites. Such a high concentration of defects is likely related to the fact that the Pt particles were not subjected to any thermal treatment following colloid preparation, contrary to traditional preparation routes. In the case of the Co-decorated sample, the Pt-multicarbonyl band was absent, supporting the analysis that the Co specifically decorated Pt sites with a low coordination number.

The particle size-dependent effect of the Co decoration, which was not observed in the case of the larger Pt particles, was attributed to the electron donation effect of the Co atoms, which modified the Pt electronic structure and created a polarized interface. This assumption

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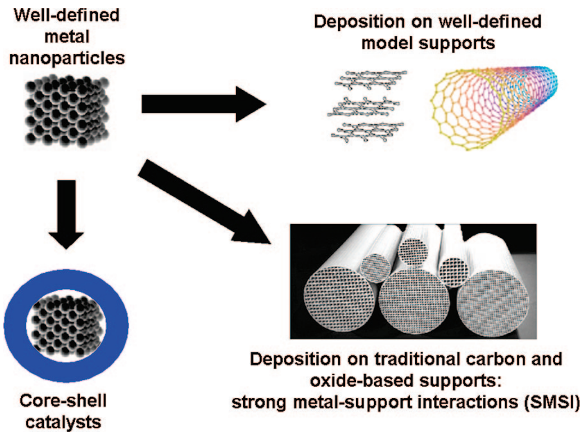
was supported by the red-shift of the vibration of the CO linearly adsorbed on Pt present on flat surfaces and by X-ray photoelectron spectroscopy analysis of the Co−Pt materials.[7] These electronic and electrostatic effects (the latter of which would influence the adsorption mode on and reactivity of the polar substrate) will naturally be greater in the case of the smaller Pt particles, while larger crystals will be essentially unaffected.

The work reported by Tsang et al.[7] emphasizes that catalysts based on colloidal metal particles are ideal model solids to investigate structure−activity relationships of metals.[7] This is especially important in the case of small nanoparticles (<5 nm) such as those produced by their methods, since those relate well to the size of traditional supported metal particles. The effects of particle size and geometry and the electronic modifications by heteroatoms on the material activity can then be independently examined. To this end, Tsang *et al*. indicated that decoration with other metals led to a range of selectivity varying in a volcano-shaped manner as a function of position in the periodic table, with Co being the optimum promoter. More detailed work will be useful in defining the position of the metal promoter atoms, possibly using atom-resolved scanning tunneling microscopy (STM) studies, which proved crucial in determining the structure of hydrodesulfurization alumina-supported MoS_2 catalysts modified by Co.[8]

Understanding the effect of the support is paramount, since a large number of applications of noble metals involve the use of large surface area and chemically reactive metal oxides, especially in the automotive and petrochemical industry.

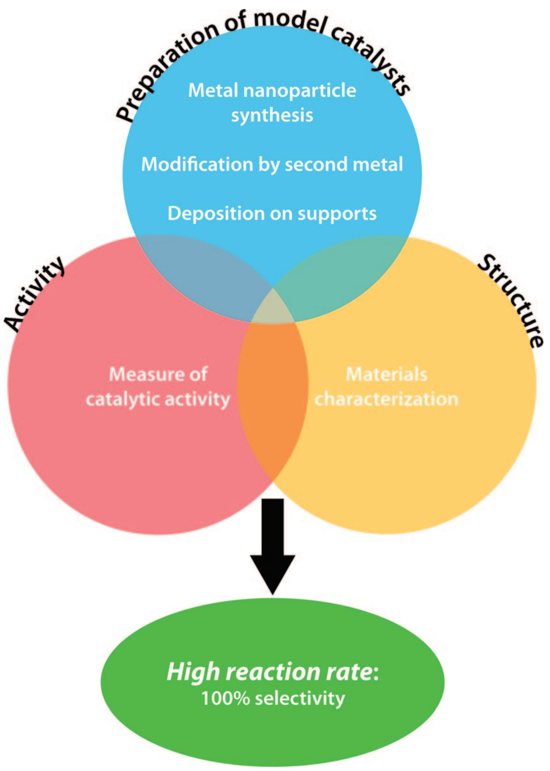
The deposition of these highly selective Co−Pt particles onto carbon-based supports led to catalysts exhibiting the same outstanding selectivity and activity.[7] The effect of more reactive supports can also be investigated, to unravel the details of potential strong metal−support interactions (SMSIs) and discriminate between size/shape effects on the one hand and support interactions on the other (Scheme 1). In fact, elucidating the exact role of oft-misnamed "inert" supports represents a lasting challenge for the catalysis community; Lambert and co-workers emphasized this point in their recent report.[5] Understanding the effect of the support is paramount, since a large number of applications of noble metals involve the use of large surface area and chemically reactive metal oxides, especially in the automotive and petrochemical industry. An understanding of the role of novel active catalytic coatings present in metal-oxide core−shell catalysts, also developed by Tsang and co-workers,[9] would also lead to the rational modification of the metallic core. Composites based on cerium oxide, showing essentially no accessible Pt metal at the surface of the "metal-in-ceria" catalyst,[10] present interesting catalytic properties that have been ascribed to electronically modified ceria.[11]



Scheme 1. The availability of well-defined metal nanoparticles should allow better understanding of the modification of the catalytic activity and selectivity depending on the features of the metal nanoparticles and the materials obtained following deposition on mostly inert well-defined supports or strongly interacting carriers. The activity of metal core−support shell composites could also be unraveled in greater detail.

Other advanced methods for the preparation of metal nanoparticles with narrow size distributions in the gas or liquid phase have recently been described. The preparation of Au particles as small as 1.5 nm was reported and based on 55-atom Au "magic" clusters.[5] Caps *et al*. proposed a new method based on laser vaporization of binary alloy rods to prepare pure Au or Au-containing alloy particles with narrow particle sizes as low as 1.5 nm.[12] Somorjai and co-workers showed that the epitaxial growth of binary Pd/Pt nanocrystals with specific shapes was possible.[13] All these methods can lead to the preparation of unsupported metal particles that can be deposited subsequently on various carriers as required for investigations of well-defined model catalysts.

The materials prepared by the techniques mentioned here are extremely useful when used as reference samples to unravel the prevailing structures of the supported metal particles under reaction conditions. This would be particularly appropriate for reactions involving CO, such as CO oxidation, the Fischer−Tropsch synthesis, and the water−gas shift reaction, since CO is a very sensitive molecular probe. The use of operando IR spectroscopy would allow comparison of the signal due to the absorption by the carbonyl present at the cata-



Scheme 2. Features for the rational design of catalysts based on model materials.

lyst surface with that on the model materials, thereby lifting the ambiguity of band assignments and revealing the true nature of the metal active sites under reaction conditions.[14] In addition to traditional supports, the nanoparticles could also be supported on carbon nanotubes, which offer well-defined and smooth surfaces for the preparation of dispersed nanoparticles. Thus, extremely well-defined model catalysts including a metallic active phase and an inert support would be available for fundamental studies.[15] In particular, these model materials should enable a better direct comparison of experimental and computational data pertaining to the structure−activity relationships of supported metals.[3,16,17]

CONCLUSIONS AND PROSPECTS

The work by Tsang *et al.*[7] epitomizes the often elusive target of catalyst developers that is the rational design of optimized catalytic materials through the understanding of the relationship between catalyst structure and activity (Scheme 2).[7] Such an achievement was possible because of the development of controlled synthesis methods for the preparation of nanometer-sized metal particles exhibiting similar shapes and narrow size distributions, relevant to those of conventional supported metal catalysts. The increasing number of synthetic methods for the preparation of well-defined nanoparticles for a wide range of metal and alloys stimulated by the developments of nanoscience and advanced characterization methods opens an exciting future for the heterogeneous catalysis community.

REFERENCES AND NOTES

1. Bowker, M. The 2007 Nobel Prize in Chemistry for Surface Chemistry: Understanding Nanoscale Phenomena at Surfaces. *ACS Nano* **2007**, *1*, 253–257.
2. Bell, A. T. The Impact of Nanoscience on Heterogeneous Catalysis. *Science* **2003**, *299*, 1688–1691.
3. Huang, W.; Ji, M.; Dong, C. D.; Gu, X.; Wang, L. M.; Gong, X. G.; Wang, L. S. Relativistic Effects and the Unique Low-Symmetry Structures of Gold Nanoclusters. *ACS Nano* **2008**, *2*, 897–904.
4. Valden, M.; Lai, X.; Goodman, D. W. Onset of Catalytic Activity of Gold Clusters on Titania with the Appearance of Nonmetallic Properties. *Science* **1998**, *281*, 1647–1650.
5. Turner, M.; Golovko, V. B.; Vaughan, O. P. H.; Abdulkin, P.; Berenguer-Murcia, A.; Tikhov, M. S.; Johnson, B. F. G.; Lambert, R. M. Selective Oxidation with Dioxygen by Gold Nanoparticle Catalysts Derived from 55-Atom Clusters. *Nature* **2008**, *454*, 981–983.
6. Bratlie, K. M.; Lee, H.; Komvopoulos, K.; Yang, P.; Somorjai, G. A. Platinum Nanoparticles Shape Effects on Benzene Hydrogenation Selectivity. *Nano Lett.* **2007**, *7*, 3097–3101.
7. Tsang, S. C.; Cailuo, N.; Oduro, W.; Kong, A. T. S.; Clifton, L.; Yu, K. M. K.; Thiebaut, B.; Cookson, J.; Bishop, P. Engineering Preformed Cobalt-Doped Platinum Nanocatalysts for Ultraselective Hydrogenation. *ACS Nano* **2008**, *2*, 2547–2553.
8. Lauritsen, J. V.; Kibsgaard, J.; Olesen, G. H.; Moses, P. G.; Hinnemann, B.; Helveg, S.; Nørskov, J. K.; Clausen, B. S.; Topsøe, H.; Lægsgaard, E.; Besenbacher, F. Location and Coordination of Promoter Atoms in Co- and Ni-Promoted MoS$_2$-Based Hydrotreating Catalysts. *J. Catal.* **2007**, *249*, 220–233.
9. Yeung, C. M. Y.; Yu, K. M. K.; Fu, Q. J.; Thompsett, D.; Petch, M. I.; Tsang, S. C. Engineering Pt in Ceria for a Maximum Metal-Support Interaction in Catalysis. *J. Am. Chem. Soc.* **2005**, *127*, 18010–18011.
10. Yeung, C. M. Y.; Meunier, F.; Burch, R.; Thompsett, D.; Tsang, S. C. Comparison of New Microemulsion Prepared "Pt-in-Ceria" Catalyst with Conventional "Pt-on-Ceria" Catalyst for Water−Gas Shift Reaction. *J. Phys. Chem. B* **2006**, *110*, 8540–8543.
11. Hardacre, C.; Ormerod, R. M.; Lambert, R. M. Platinum-Promoted Catalysis by Ceria: A Study of Carbon Monoxide Oxidation over Pt(111)/CeO$_2$. *J. Phys. Chem.* **1994**, *98*, 10901–10905.
12. Caps, V.; Arrii, S.; Morfin, F.; Bergeret, G.; Rousset, J.-L. Structures and Associated Catalytic Properties of Well-Defined Nanoparticles Produced by Laser Vaporisation of Alloy Rods. *Faraday Discuss.* **2008**, *138*, 241–256.
13. Habas, S. E.; Lee, H.; Radmilovic, V.; Somorjai, G. A.; Yang, P. Shaping Binary Metal Nanocrystals through Epitaxial Seed Growth. *Nat. Mater.* **2007**, *6*, 602–607.
14. Daly, H.; Ni, J.; Thompsett, D.; Meunier, F. C. On the Usefulness of Carbon Isotopic Exchange for the Operando Analysis of Metal−Carbonyl Bands by IR over Ceria-Containing Catalysts. *J. Catal.* **2008**, *254*, 238–243.
15. Javey, A. The 2008 Kavli Prize in Nanoscience: Carbon Nanotubes. *ACS Nano* **2008**, *2*, 1329–1335.
16. Nigam, S.; Majumder, C. CO Oxidation by BN-Fullerene Cage: Effect of Impurity on the Chemical Reactivity. *ACS Nano* **2008**, *2*, 1422–1428.
17. Gao, Y.; Shao, N.; Zeng, X. C. Ab Initio Study of Thiolate-Protected Au$_{102}$ Nanocluster. *ACS Nano* **2008**, *2*, 1497–1503.