**Nanocatalysis**

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# Nanocatalysis Beyond the Gold-Rush Era[**]

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Sabatier analysis

Heterogeneous catalysis contributes to the creation of a very large fraction of global economic wealth. In particular, heterogeneously catalyzed reactions are at the center of energy production, pollution remediation, and the production of chemicals and pharmaceuticals.[1] A significant number of heterogeneous catalytic processes are performed by transition-metal catalysts supported on metal oxides. Several of these metals belong to the platinum group and are quite expensive. Therefore, if smaller amounts of these metals could be utilized, significant cost reductions in technological processes might be achieved. With this motivation, scientists and engineers have studied particle-size effects in catalysis for a number of years.[2] There are several key issues to be considered: 1) The relative abundance of low- and high-coordinate sites changes as a function of particle size.[3] 2) Metal–support interactions might change with particle size.[4] 3) The electronic structure of very small metal particles might exhibit quantum size effects.[5]

Particle-size effects have been studied for various combinations of reactions and active metals, mainly to elucidate the structure sensitivity of these reactions, but for the last twenty years, the main focus of nanocatalysis has been on studying the reactivity of small gold nanoparticles. Gold has been one of the most precious metals for mankind for thousands of years. Because of its resistance to oxidation, it has been primarily used for monetary exchange and jewelry fabrication. However, in the late 1980s, Haruta et al. discovered that gold nanoparticles smaller than 5 nm (see Figure 1) supported on α-$Fe_2O_3$ are very active for CO oxidation, a reaction of key technological importance, far below room temperature.[6] The unprecedented level of research activity undertaken by the catalysis community right after that discovery to explain and capitalize on gold catalysis could easily justify the name "Gold-Rush Era" in heterogeneous catalysis. Despite this intense activity, several of the key questions pertaining to gold nanocatalysis, for a variety of reactions well beyond CO oxidation, are still under intense debate.[7]

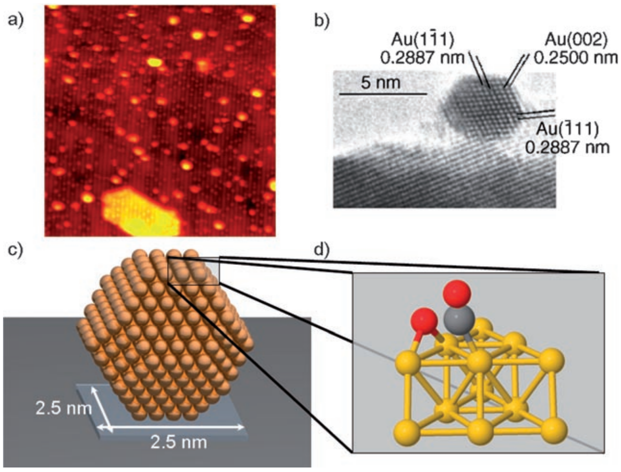

***Figure 1.*** Catalytic nanoparticles at various levels of detail: a) STM image of Au nanoclusters on oxidized $TiO_2$(110). Reproduced from reference [8]. Reprinted with permission from AAAS. b) TEM image of Au on ZnO calcined at 400 °C showing a 5 nm cuboctahedral Au nanoparticle. Reproduced from reference [9]. c) Model of a 2–3 nm cuboctahedral gold nanoparticle. d) Schematic illustration of the transition state for CO oxidation on a 12-atom cluster used by Falsig et al.[10] to represent the low-coordinated atoms at the corners of cuboctahedral metal nanoparticles.

Falsig et al. use a combination of planewave density functional theory (DFT) calculations and kinetic modeling to rationalize catalytic reactivity trends on both extended surfaces and nanoparticles of several metals for CO oxidation.[10] They establish a unifying framework for the analysis of this reactivity on both types of sites and explain the origin of the unique catalytic properties that gold nanoparticles possess for that reaction.

DFT calculations have become the method of choice to derive the energetics of surface processes,[11] but to calculate reaction rates, these energetics need to be used in either detailed microkinetic models[12] or kinetic Monte Carlo simulations.[13] Both approaches are quite demanding. Among the attractive features of the work by Falsig et al. is their implementation of a very simple yet powerful approach that does not require the full solution of a microkinetic model or extensive kinetic Monte Carlo simulations but rather relies on the use of an approximate Sabatier analysis.[14,15]

The Sabatier analysis is by no means a replacement for a microkinetic model or kinetic Monte Carlo simulations, but it is particularly useful for establishing reaction-rate trends in

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catalysis. More specifically, the Sabatier reaction rate is the maximum rate that can be achieved under the assumption that all surface coverages are "optimal". These optimal coverages may not always be realistic, but the Sabatier analysis provides an exact upper bound on the reaction rates. Figure 2 demonstrates how catalytic reaction rates vary as a function of a key reactivity descriptor, such as the binding energy of an important reactive intermediate. For a specific reaction, strong binding of that intermediate may lead to surface poisoning, whereas weak binding may lead to limited availability of the intermediate; in both cases, catalytic rates are less than optimal. The abscissa corresponding to the top of the resulting volcano rate curve marks the optimum value of the reactivity descriptor. Naturally, identifying the key reactivity descriptor is very important. Through detailed DFT work on several extended surfaces and nanoparticles (Figure 1 c, d) Falsig et al. managed to single out two such descriptors for the CO oxidation reaction: the binding energy of CO and that of atomic oxygen. All other thermochemical and kinetic parameters appearing in the detailed reaction network can be correlated to these two parameters. Subsequently, they calculated the Sabatier reaction rates by scanning a 3 eV range of values for these two binding energies, and they found that for extended metal surfaces, platinum and palladium give the maximum CO oxidation rates, whereas for small nanoparticles gold is the most active metal.

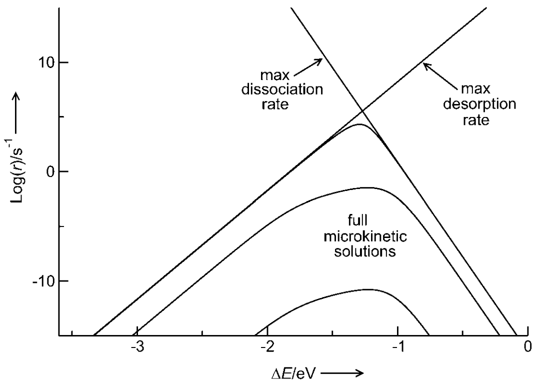

***Figure 2.*** Schematic volcano plot for the reaction rates (*r*) predicted by 1) the solutions of a full microkinetic model under different reaction conditions and 2) the approximate Sabatier rates, both as a function of an appropriate reactivity descriptor, in this case the dissociative chemisorption energy Δ*E* of a key reactant. Reproduced with modifications from reference [15].

These results are exciting for several reasons: 1) They are in complete agreement with prior experiments, suggesting that a generalized methodology for identifying promising catalytic sites for various heterogeneously catalyzed reactions has now been established. 2) They show that there is no magic about small gold nanoparticles in connection to the CO oxidation reaction; these nanoparticles simply possess very potent under-coordinated sites with the optimal binding for CO and O at the right reaction conditions. Previous research has shown that many factors could be implicated in the unusual reactivity of gold nanoparticles,[4–7] but this work has clearly isolated one of these factors and its dominant effect.

The approach presented by Falsig et al. provides a simple, unifying framework for linking catalysis observed on extended surfaces, typical model systems for surface science, and on small nanoparticles, representative of realistic supported industrial catalysts. However, the extension of this approach to reactions more complicated than CO oxidation may prove to be a significant challenge. CO oxidation is rather simple, and all possible elementary reaction steps can easily be accounted for, including mechanistic changes as a function of reaction conditions and metal identity, possibly extending to cases in which metal oxide formation might play a role. For more complicated reactions, such as catalytic conversion of biomass derivatives to fuels and chemicals,[16] reaction mechanisms can vary drastically with different metals and reaction conditions. In situations like these, identifying the correct reactivity descriptors, going beyond what intuition can suggest, might be more challenging. In addition, special catalytic site compositions[17] might offer opportunities for deviating from universal relations connecting thermochemistry and kinetics of key bond-breaking or bond-making events, thus offering exciting opportunities for novel catalyst development. Extending this new approach to include these and other possibilities will be most desirable.

Last, but not least, the findings of Falsig et al. open up great new opportunities, well beyond CO oxidation, for other catalytic reactions for which gold nanoparticles would be inactive, but perhaps other metal (e.g. ruthenium, cobalt, or nickel) nanoparticles could be orders of magnitude more reactive than standard, currently used, large catalytic particles of other precious metals. Moving to nanoparticle catalysis, combined with ways to stabilize those nanoparticles against sintering, holds the promise of utilizing smaller amounts of metal, which, in turn, could lead to considerable process cost reductions. If the catalysis community has been nearly obsessed with gold nanoparticles over the last twenty years, this elegant contribution may lead to several more productive years of research into nanocatalysis in general, going well beyond the "Gold-Rush Era" in catalysis.

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