Catalysis Today 160 (2011) 1–2

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Preface

Heterogeneous catalysis by metals: New synthetic methods and characterization techniques for high reactivity

Heterogeneous catalysts are utilized in a variety of industrial processes and technologies making them the subject of intense research in order to understand how to optimize their functionality. They are often multi-component materials with each component having a particular function, and comprised of catalytically active components over large length scales—from chemical bonds (Å) to microns (i.e., catalyst pellets). The study of the structural, dynamic, and reactive behavior of catalysts requires methodologies to synthesize uniform catalytic structures and techniques capable of resolving the structure—at least to some extent—of the catalysts over these length scales, ideally with energy, spatial and temporal resolution. A common approach is to synthesize simple models of these seemingly complex materials and characterize these simpler systems with techniques of increased resolution. The knowledge learned from these studies should provide the information required for rational catalyst design. Rational design of catalyst relies on the ability to build catalytic materials with increasing complexity (from the single crystal on).

The idea of this special issue of *Catalysis Today* was born out of a fruitful discussion with Professor Julian Ross. The concept of this issue was to combine recent advances in synthesis methods and characterization techniques of metal-based heterogeneous catalysts from experimental to theoretical approaches, encompassing both classical (supported) and model catalysts. This special issue provides the catalysis community with some of the newest developments in approaches to catalyst synthesis and the application of state-of-the-art characterization techniques, such as X-ray-based techniques (absorption, scattering, diffraction), molecular beam scattering, high-resolution electron/probe microscopy, 3D electron tomography, solid-state nuclear magnetic resonance spectroscopy, and first-principles theoretical calculations.

The synthesis of heterogeneous catalysts has long been considered more of an art than a science. Starting with a supported Pd catalyst synthesized by traditional preparation methods, Rebelli et al. have demonstrated that various metals, such as Ag, Au, and Cu can be selectively deposited on Pd impregnated on a SiO_2 support by electroless deposition (ED). Judicious optimization of the ED bath conditions allows the metals to be deposited on Pd with incremental coverage. For some metal–Pd combinations, ED deposition discriminates against the exposed surfaces on the Pd crystallites; while for other metal–Pd combinations, deposition of the second metal on the Pd crystallite is indiscriminate. These ED-produced catalysts are characterized by classic, yet very useful techniques, such as FTIR spectroscopy and X-ray photoelectron spectroscopy to determine the surface coverage of Pd and the overall electronic structure of the bimetallic catalysts, respectively. The preparation of colloidal nanoparticles for applications in catalysis has provided the ability to tune the structure and composition of nanoparticles with unprecedented control. The paper by Fang et al. and Yin et al. are two examples of the modification of colloidal nanoparticles synthesized in solution by the subsequent deposition of a second metal on pre-formed nanoparticles to form core–shell particles. In the work by Yin et al., they demonstrated that Au nanoparticles covered with a Fe_2O_3 shell of varying thickness by the thermolysis of iron pentacarbonyl onto the surface of alkylthiol-protected Au nanoparticles were highly active and stable for low-temperature oxidation when deposited on traditional catalyst supports. Fang et al. used a reduction procedure to deposit Pd on pre-formed Au nanoparticles. Au nanoparticles covered with 0.6 ML of Pd were more active than monometallic catalyst for the complete hydrodechlorination of trichloroethylene to ethane in aqueous solution. The origin of enhanced activity of the Pd/Au core–shell particles is not yet known, although the authors believe it is related to the enhanced oxidation resistance of Pd in the presence of Au. Synchrotron-based methods, such as X-ray absorption near edge structure (XANES) and extended X-ray absorption spectroscopy (EXAFS) are powerful techniques for the characterization of catalysts. Fang et al. utilized a combination of XANES/EXAFS to confirm that a fraction of the Pd remained metallic in the PdAu core–shell nanoparticles upon exposure to air, and that the structure of the PdAu particle was core–shell with the surface present as a homogeneous PdAu alloy. Vicente et al. used a high energy resolution fluorescence based X-ray absorption spectroscopy (HERD XAS) technique to resolve subtle details in electronic structure for Pt and PtSn supported in zeolite L and Al_2O_3. The features of HERFD XAS spectrum are sharper and better-defined than in a typical XANES spectrum, providing more information about the influence of support and alloying of a second metal with Pt on the electronic structure of the supported Pt. They determined that a bimetallic Pt-Sn catalyst supported on zeolite L had an electronic structure that was more similar to Pt/Al_2O_3 than Pt/zeolite L. The catalysts with similar electronic structure also displayed similar behavior during the oxidation of carbon monoxide. In a combined experimental and theoretical study, Molina et al. used a size-selected cluster source to deposit Ag nanoparticles with diameters ranging from 9 to 23 nm onto amorphous Al_2O_3 planar substrates. The two-dimensional model catalysts were active for the partial oxidation of propylene; particles with an average diameter of 9 nm were selective for acrolein production, while larger particles (>20 nm) were selective for propylene oxide. The authors complemented the experimental study with first principle

0920-5861/$ – see front matter
doi:10.1016/j.cattod.2010.09.001

calculations to discern the influence of nanoparticle morphology on the competing reaction pathways. The barriers determined from theoretical conditions were in accord with experimental observations. The combination of first-principles density functional theory (DFT) calculations of adsorption and reaction energetics and experiments provide significant insight into what properties of the catalyst enable the attainment of high activity and selectivity.

Metal-based planar model systems—usually investigated under ultrahigh vacuum (UHV) conditions and frequently complemented by DFT calculations—have yielded significant insight into the fundamental aspects of catalytic reactions at the atomic/molecular level. An integrated approach, which combines modern surface techniques with traditional methods, can significantly enhance our understanding of a broad range of phenomena that occurs on metal surfaces impacting reactivity and selectivity. Rodriguez et al. employ *in-situ* X-ray absorption measurements to discover the active phase of Au nanoparticles supported on ceria or titania single crystals or films for the water-gas shift reaction, which consists of metallic nanoparticles of gold on a partially reduced oxide support. The adsorption and dissociation of water take place on the oxygen vacancies of oxides, while CO adsorbs on the gold nanoparticles; all subsequent reaction steps occur at the oxide–metal interface. Mullins and co-workers apply molecular beam reactive scattering and isotopic exchange experiments to understand the reaction between water and clean and oxygen pre-coverered single-crystal metal surfaces. Water dissociates on the clean iridium surface with a low probability (10^{-2} to 10^{-3}), and the presence of pre-covered oxygen causes a strong interaction between water and the Ir surface. Temperature-programmed reaction spectroscopy is widely used to obtain information on the nature of adsorbate species as well as adsorption energies and surface structure. Weaver and colleagues demonstrate that this technique combined with DFT calculations can be used to probe the reaction mechanism of alkanes on metal oxides films epitaxially grown on metal single crystals. For example, *n*-butane undergoes C–H bond cleavage on PdO(101) and the resulting fragments are oxidized completely upon heating. Theoretical investigations of catalytic reactions on model surfaces is continued with several other topics such as hydrogenation of benzene on Ru(0001) (Fan et al.), dissociation of carbon monoxide on Mn modified Rh(111) and Rh(553) (Ma et al.), and the synthesis of hydrogen peroxide on Pd, Pt, and Au surface (Djordjevic and Meyer).

This issue demonstrates the combination of advanced experimental approaches and electronic structure theory brings great precision to heterogeneous catalysis, validating and extending previous assumptions in the field. Thirty papers appear in this special issue of *Catalysis Today*. The Guest Editors would like to thank all the authors for their excellent contributions and the referees for their dedication and responsibility. We also acknowledge Professor Julian Ross and Professor Yongdan Li for their valuable advice and cooperation, and Ms. Mary Harty and Ms. Rosie Malone for their assistance in preparing this issue. One of the guest editors (J.L.G.) is grateful to Professor George Whitesides (Harvard University) for his advice and sage counsel.

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24 August 2010