Heterogeneous Catalysis

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Probing Solid Catalysts under Operating Conditions: Electrons or X-rays?**

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Two recent, significant advances[1,2] in the realm of in situ studies of heterogeneous catalysis highlight afresh the competing advantages and limitations of electrons on the one hand, and X-rays (from synchrotron sources) on the other as probes of choice for investigating solid catalysts at work. One reports[1] atomic-scale electron microscopy at ambient pressure, and the other describes[2] nanoscale imaging of a working catalyst by scanning transmission X-ray microscopy (STXM). In assessing the importance of these reports it is prudent to recall that a principal aim of in situ studies of catalysts is to deduce what clues are provided so as to be able to design new, superior catalysts:[3] it is not simply to determine what action—atomic, molecular, or nanoparticulate—takes place during the course of catalytic turnover, important as this is.

Insofar as post mortem (or pre natal) studies of solid catalysts are concerned, few techniques rival electron microscopy, whether by high-resolution transmission (HRTEM) or by high-resolution scanning transmission (HRSTEM).[4] Each of these, in its numerous modes of operation, yields structure (in atomic detail), crystallographic phase, chemical composition, morphology and, under favorable circumstances, even bond distances and oxidation states of constituent chemical elements—all at high spatial resolution. But because the mean free path of electrons is minute at atmospheric pressure, it is extremely difficult to study gas/solid interactions, still more so solid/liquid ones under conditions typical of those that prevail in almost all industrial applications of heterogeneous catalysis. Over the years, however, successful efforts have been made, following the pioneering work of Gai et al.[5–7] to perfect so-called environmental TEM (ETEM) systems.[8] Through differential pumping and other adroit modifications to both custom-built high-voltage [e.g. 1000 kV; high-voltage electron microscopy (HVEM)] and commercial microscopes operating up to 200 kV, atomically-resolved images of supported metal catalysts (typically Pt on TiO_2) operating with H_2 pressures of approximately 3 mbar in the range 300 to 450 °C may be recorded in situ. After achieving 5 Å resolution in studying MoO_3 oxidation catalysts,[5] Gai an co-workers later produced high-resolution images of the microporous selective oxidation catalyst Mn ALPO-18 at 0.5 bar of H_2.[9]

Although supported nanoparticle catalysts with predefined shapes can be routinely synthesized, there is no guarantee that such materials remain stable when exposed to the reaction conditions of catalysis. Gaseous reactants often induce changes in surface and interfacial energies[8] and hence drive re-structuring of the nanoparticles, thereby influencing the nature of the resulting catalytic activity and selectivity. Dramatic changes of the shape of remarkably catalytically active Au nanoparticles occur when low pressures of O_2 or H_2 surround them even at room temperature.[8]

Creemer et al.[1] have ingeniously shown how ETEM may be used to watch catalysts at work by exploiting the technology of micromechanical systems (MEMS). They limited the number of gas species in contact with the specimen in the microscope, even at an atmosphere pressure, by designing a novel nanoreactor that has micrometer-sized gas-flow chambers and electron-transparent windows (of SiN_x in its amorphous state). Also, by using a special heater, Creemer et al. conducted variable-temperature experiments on a sub-second time scale. In a proof-of-principle test on the methanol synthesis (and water-gas shift) catalyst, namely Cu/ZnO, they observed directly the growth of the Cu nanoparticles during heating to 500 °C and exposure to 1.2 bar of H_2. Their nanoreactor seems versatile enough to cope with other gaseous environments and possibly with liquid reactants just as was done by Gai et al. in their microscopic study of the liquid phase hydrogenation of adiponitrile to hexamethylene diamine, a key component of nylon (6,6). Through their ETEM studies, Gai et al.[8] contributed to the development (by the Du Pont Co.) of improved commercial catalysts for this hydrogenation.

Nanoreactor cells suitable for in situ characterization of solid catalysts by soft X-rays[10] and by hard X-rays[11] have previously been described. Those suitable for exploration by hard X-rays could routinely cope with liquid environments as well as enabling product analysis during catalysis (by GC/MS methods).[11] The nanoreactor of Creemer et al. is not yet that versatile but it was admirably suited for the recent nanoscale

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imaging of a working catalyst by STXM reported by de Smit et al.,[2] whose approach uses a Fresnel-type zone plate to focus monochromatic X-rays down to a spot size of 100 to 200 Å. By scanning through different X-ray energies (at the Berkeley Advanced Light source) and traversing the X-ray absorption edges of known elements in the catalysts they mapped the absorption across the solid, thereby arriving at an "image" of the spatial distribution of each element. They found that the minute particles of Fe_2O_3 dispersed initially over SiO_2 (to simulate a Fischer–Tropsch catalyst for converting CO + H_2 mixtures into hydrocarbons) were converted at reaction temperatures up to 350 °C and a pressure of one bar into metallic iron, some iron carbide, and Fe_3O_4 as well as some Fe_2SiO_4. The spatial distribution (150 Å) of their technique is impressive, but it is not capable of yielding a truly atomic-scale view of the structure of the working catalyst. Improvements in detector design will, in turn, permit time-resolved experiments; and the authors opine that their approach may in future allow in situ studies of solid catalysts in contact with liquid environments.

If monophasic, single-component solid catalysts (into which spatially-separated active sites have been incorporated, like Ti^{IV} centers in mesoporous silica, epoxidation catalysts) instead of multiphasic, multicomponent catalysts are studied in situ with hard X-rays, penetrating insights into the nature of the active sites are revealed.[11] As summarized in Figure 1, the precise structure of the active site, prior to, during, and after catalytic turnover, is derived from the in situ X-ray absorption spectra and parallel in situ Fourier transform infrared (FTIR) analysis.[11] A knowledge of the mechanism of the catalytic reaction and mode of operation of the catalyst emerges; and this information formed the basis for the design of improved variants of the catalyst.

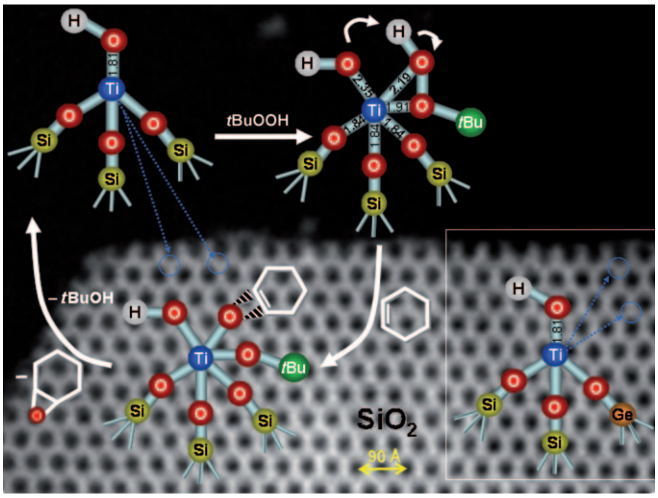

Figure 1. In situ extended X-ray adsorption fine structure spectroscopy (EXAFS) studies reveal the structure of the empty active site (a titanol group tripodally attached to mesoporous silica, top left) for the epoxidation of cyclohexene. The steady-state structure is sixfold coordinated (center) from which the mechanism may be deduced. It is of the Eley–Rideal kind; only one of the two reactants (the *t*BuOOH) is adsorbed. The "free" cyclohexene plucks an oxygen atom from the hydroperoxide chemisorbed at the active site. When HOTi$-(OSi)_3$ active centers are replaced by HOTi$-(OSi)_2(OGe)$ (bottom right) a superior catalyst results.

An in situ approach of this kind, through X-ray absorption, has more than a superficial kinship with the in situ study by Phillips[12] who, by X-ray single-crystal X-ray diffraction, solved the structure and mode of action of the enzyme lysozyme.

The technical virtuosity of the in situ experiments of Creemer et al.[1] and de Smit et al.[2] prompts us to assess the relative merits of synchrotron radiation and electron microscopy as a means of probing the characteristics and elucidating the chemistry of solid catalysts encompassing both inorganic and biological ones.

Synchrotons Versus Electron Microscopes

In favor of the X-ray approach towards probing catalysts in situ are the following key features:

- high fluxes (of both nonfocused and nanofocused) of monochromatic as well as high fluxes of polychromatic X-rays;
- high penetrating power of (high-energy) synchrotron radiation so that thick specimens and those in contact with liquids may be readily investigated;
- high degree of energy resolution (ca. 0.1 eV);
- ease of effecting X-ray microscopic tomography of both small and large specimens, coupled with the advantage of being able to determine the chemical composition from X-ray absorption peaks of the catalyst through the tunability of the wavelength;[13–15]
- the in-principle possibility of combining the recently developed technique of coherent diffraction imaging (CDI; or diffraction imaging microscopy (DIM)—these two acronyms signify the same principle) and STXM, using nanofocused illumination;[14,16,17]
- high brightness of the infrared region of synchrotron radiation also allows considerable scope for in situ microspectroscopic studies of catalytic reactions taking place in nanoporous solids—see, for example, the work of Stavitski et al.[18] on the oligomerization of styrene derivatives at single-site Brønsted acid, active centers. Necessarily the spatial resolution in such work is not high (2 to 10 μm) and incapable, therefore, of affording mechanistic insights;
- the feasibility of combining wide-angle, small-angle, and ultra-small angle X-ray scattering (WAXS, SAXS, and USAXS, respectively) for the direct imaging of open-structure and hybrid catalysts as demonstrated by Peter-Paul et al.[19]

Already polychromatic synchrotron radiation has contributed enormously to the dynamic events that occur in the operation of certain proteins. Laue crystallography, for example, has elucidated the individual six intermediate states and the overall reaction pathway in the room temperature photocycle of the photoactive yellow protein from nanoseconds to seconds.[20] In addition, the recent availability of ultrasensitive X-ray CCD cameras enables the changing chemical composition (and oxidation states) of polycrystalline catalysts inside a glass reactor tube (under commercially realistic conditions) to be probed with commendable spatio-temporal resolution by Grunwaldt et al.[21]

The principal disadvantage of X-rays as primary probes, however, is their relatively large beam cross-section, which is several orders of magnitude more than that of very sharply focused (ca. 2 Å diameter) high-energy electrons. It follows that spatial characterization with X-rays cannot compete with that attainable using STEM. But, like positron emission computerized tomography (PET),[22] or magnetic resonance imaging (MRI),[23] it is well-suited for the in situ investigation of catalysts operating in reactors typical of those used industrially.

In favor of the electron approach for in situ studies is the wealth of information that is provided both by STEM and TEM, quite apart from their vastly superior spatial resolution. These include:

- high-angle annular dark-field imaging with its ability to highlight (through Rutherford scattering) the precise three-dimensional spatial location of heavier elements dispersed on light supports from STEM tomography;[14]
- electron-stimulated X-ray emission with the senstivity to detect clusters of a dozen or so atoms (e.g. 10^{-21} g of $Ru_{10}Pt_2$ on silica);
- the whole energy range provided in electron-energy-loss spectroscopy (EELS)—from plasmon peaks, through near-edge regions corresponding to core-electron EELS [i.e. electron-loss near-edge structure (ELNES)], which carry information which reveals the coordination finger-printing[24] of certain groups such as BO_3, AlO_4, AlO_6, SiO_4, and SiO_6;
- ELNES spectra and white-line intensities in EELS often yield reliable information pertaining to, respectively, bond lengths and oxidation states, particularly of transition-metal ions.[14]

No attempt has yet been made to deploy, for in situ studies of solid catalysts, the revolutionary four-dimensional electron microscopy approach pioneered by Zewail and co-workers[25] that has made enormous improvements—in some cases by some ten orders of magnitude—to time-resolved microscopy. There is little doubt that the mechanistic details of single-site photocatalysts will be amenable to the kind of dramatic technical advances reported from the Zewail group in their four-dimensional imaging of transient structures and morphologies of nanogold and nanographite,[25] thereby yielding hitherto unprecedented information about the dynamics of catalytic turnover at such solid surfaces. With infrared excitation, thermally-activated solid catalysts of the kind described above will be readily amenable to the Zewail four-dimensional approach, using a T-jump. The judicious use of temporal nanoscale cooling and heating of the kind achieved with gold films,[25] if successful, should yield altogether new information about restructuring of the topography of solid catalysts and their chemical consequences. Delivering the excitation through electron heating may result in different pathways of reactivity as electrons may become part of the femtochemistry on the surface.

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