

Probing Solid Catalysts Under Operating Conditions

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Most of the techniques used to characterize the surfaces or to probe the nature of the active centers of solid catalysts are far better suited for examination of model rather than actual catalysts. Techniques such as ultraviolet- and x-ray-induced photoelectron spectroscopy, Auger-electron and electron-energy loss spectroscopy, photoelectron diffraction, and photoemission and high-resolution electron microscopy often require that the surfaces under investigation be held in high vacua. Secondary ion mass spectrometry, as well as ion beam scattering procedures, likewise demands comparable, rarefied conditions.

ideal technique or subset of techniques ought to be able to track changes in composition, valence state, bonding, coordination, and crystallographic phase. Moreover, it should be usable during widely varying thermal or other excursions starting with the precursor material and the changes it undergoes through its process of activation (usually heating in a controlled atmosphere), its operation as an active catalyst, its poisoning (if any), its gradual or sudden loss of activity and specificity, and its subsequent regeneration by oxidation or exposure to an appropriate gas.

Synchrotron radiation's supreme advan-

tions of EXAFS (or XANES or PEXA) and XRD in a combined manner on a time scale of seconds, depending on the nature of the catalyst (or catalyst-support system) under consideration. Moreover, such in situ studies may now be routinely conducted at temperatures up to 1200°C (3).

The entire powder diffraction (XRD) pattern of a catalyst may be continuously monitored during the course of its activation, operation, and decline (4–6). At the same time, there is merit to the use of the energy-dispersive mode for recording with EXAFS the dynamics of the structural changes accompanying the thermal activation of a catalyst (7). With a photodiode array for the recording of x-ray absorption signals and a position-sensitive detector (PSD) for XRD, one can trace changes in both short-range and long-range crystallographic order during the entire course of the production of an active metal catalyst from its compound precursor. Specifically, we and our colleagues have studied (4, 8) synthetic variants of the mineral phase aurichalcite $[\text{Cu}_{5-x}\text{Zn}_x(\text{OH})_6(\text{CO}_3)_2]$, a layered hydroxycarbonate with Cu/Zn ratios ranging from 0.25 to 1.00. Specimens were heated in air to 450°C in a special cell attached to gas-analytical facilities to yield mixed oxides of Cu and Zn, which were then reduced to produce ZnO-supported metallic Cu that could be probed by EXAFS and XRD while functioning as an active catalyst for the water gas shift reaction ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$) [this catalyst is closely akin to the Imperial Chemical Industries (ICI) commercial catalyst for the production of methanol from synthesis gas]. In the early stages of the thermal treatment of the aurichalcite, no significant changes occur in the local environment of Cu(II) species even though there are drastic changes in crystallinity of the solid precursor as it is heated to drive away water and CO_2 and to break down the parent layer structure. We found no evidence of assimilation of Cu(I) species into the ZnO, but there was clear evidence of some incorporation of Zn into the metallic Cu forming a dilute, disordered phase of brass.

An alternative setup (3, 4, 9, 10) that has been used to track structural changes entails recording "quick" EXAFS (QuEXAFS) with the aid of a rapidly scanning monochromator and XRD patterns, again by use of a PSD. Debye-Scherrer x-ray patterns from complex catalysts such as metal-ion-exchanged zeolites may be routinely obtained in about 400 s with a resolution of $\sim 0.04^\circ$ in 2θ . With the high-flux station 9.3 at the SRS Daresbury facility, EXAFS spectra can be collected either in fluorescence or transmission mode in scan times of between 10 and 300 s (comparable with the times to accumulate XRD patterns).

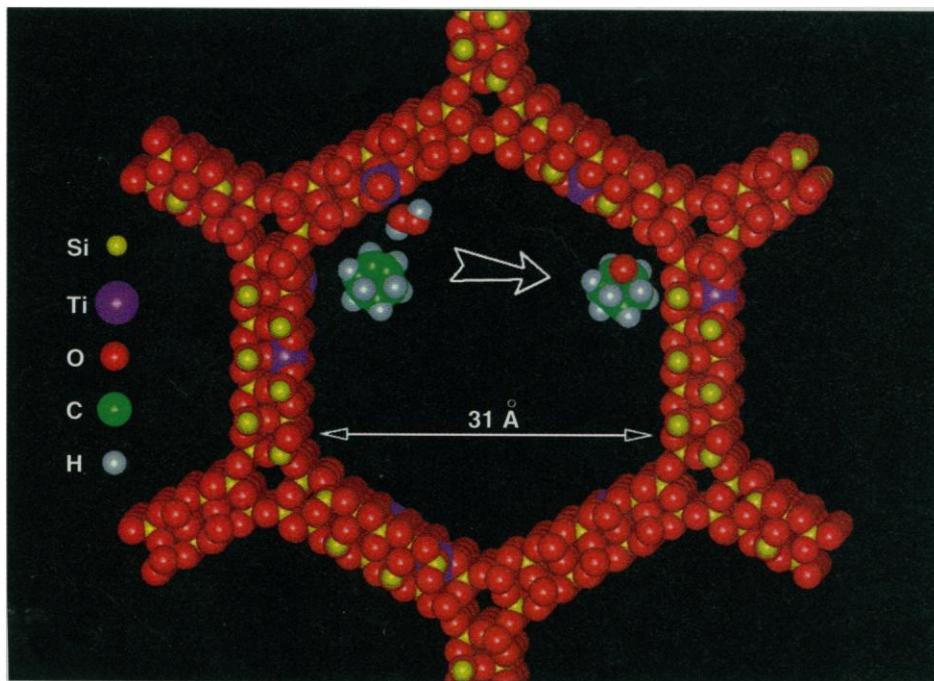


Fig. 1. The liquid-phase epoxidation of cyclohexene in the presence of H_2O_2 , catalyzed by a mesoporous titano-silica.

Despite significant progress with techniques such as scanning probe microscopy, infrared spectroscopy, confocal laser microscopy, sum-frequency generation, and neutron scattering, it is unlikely that any of these hold promise for the study of complex polycrystalline catalysts. To be sure, the

tage (1, 2) is that it permits the ready retrieval of short-range (radii $\sim 8 \text{ \AA}$) atomic order and coordination numbers [from x-ray absorption near-edge structure (XANES), extended x-ray absorption fine structure (EXAFS), and pre-edge x-ray absorption (PEXA)], as well as quantitative information about crystallographic integrity and long-range order [from x-ray diffraction (XRD)]. As outlined below, it is very convenient with available sources of synchrotron radiation to conduct in situ time-resolved and variable-temperature investiga-

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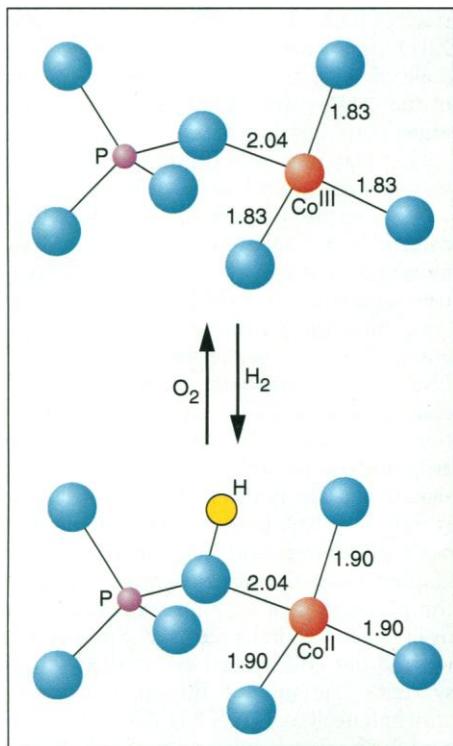


Fig. 2. Bond lengths from combined XRD-EXAFS in situ studies at the active site in a CoALPO (cobalt aluminum phosphate) catalyst for converting methanol to alkenes [adapted from (12)].

We have illustrated (8) the power of the combined EXAFS-XRD technique for tracking catalysts under operating conditions and also for tracking the formation of catalyst supports at elevated temperatures. The catalyst that we recently investigated in situ is a member of a large family of molecular sieves in which minute amounts of cobalt are framework-substituted in place of aluminum in the open structure of a synthetic aluminum phosphate known as ALPO-18 (11). These solid acid catalysts [$H_x(\text{Co}_x\text{Al}_{1-x})\text{PO}_4$, with x ranging up to 0.04] efficiently convert methanol to light olefins (predominantly ethene and propene). Combined in situ XRD and cobalt K-edge EXAFS studies (12) recorded both during calcination and reduction have revealed (Fig. 2) simultaneous changes in bond lengths and oxidation state of the active center in the Co-ALPO-18 catalyst. In particular, all of the redox changes that occur around the cobalt in the catalyst when it is calcined in O_2 and then reduced in H_2 to generate Brønsted acidity take place around 350°C , which is the temperature marking the onset of catalysis.

Cordierite (idealized formula $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) is the principal support material for the platinum group metals (Rh, Pt, and Pd), in the so-called "three-way" autoexhaust cata-

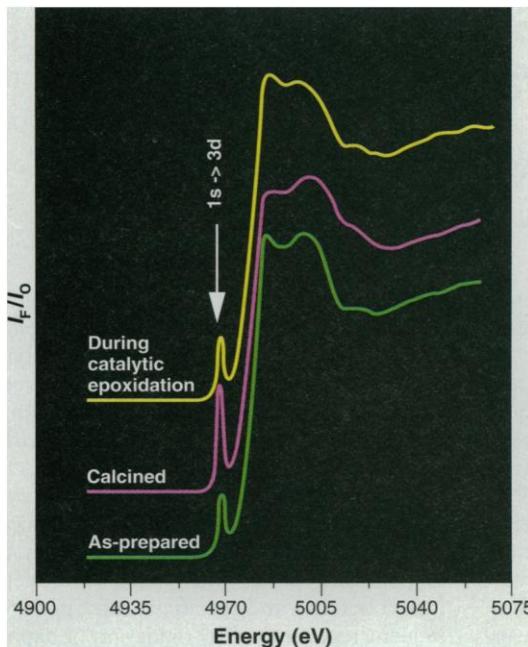


Fig. 3. EXAFS data from the system illustrated in Fig. 2 [adapted from (14)].

lyst. Using our combined QuEXAFS-XRD in situ procedure, we have tracked (3) the detailed structural changes accompanying the conversion of Mg^{2+} exchanged zeolite B, through an amorphous and then through a stuffed quartz phase, to crystalline cordierite at temperatures of $\sim 1050^\circ\text{C}$. Traces of ZnO catalyzed the solid-state conversion of the zeolite precursor to the cordierite (13).

Probing the atomic environment of active sites in solids that catalyze reactions in the liquid state is also feasible (14), thanks to synchrotron radiation, under favorable circumstances. By means of a special cell that accommodated a thin layer ($\sim 10 \mu\text{m}$) of liquid reactants—aqueous H_2O_2 in the presence of cyclohexene (15)—changes in the x-ray absorption near-edge and pre-edge structures of titanium in a titano-mesoporous siliceous catalyst (Fig. 1) derived from the recently discovered MCM-41 family of mesoporous "crystalline sponges" (16, 17) were recorded. This was done in fluorescence mode with an ultrasensitive, multielement solid-state detector (18). Typical results (Fig. 3) are amenable to quantitative analyses, yielding precise values for Ti-O distances in the as-prepared, the calcined, and the operating (active) catalyst (14).

Many of the in situ experiments summarized above could be improved in quality and executed much more rapidly by access to some of the new and certainly to future generations of synchrotron sources. Already at the European Synchrotron Radiation Facility in Grenoble, thanks to technical

advances in the design of undulators with low-emittance electron beams and in x-ray optics (19, 20), a brilliance of 10^{19} photons per second is already achievable, making it possible to record Laue diffraction patterns from micrometer-sized crystals in 40 ps, with a repeat every microsecond or so (19). Corresponding improvements in x-ray solid-state detector design and data handling mean that it is already practical to probe the environments of elements in solids at the 10 parts per million impurity level exploiting fluorescence EXAFS (21). Moreover, with existing semiconductor fabrication technology, the detection and transfer of two-dimensional x-ray images of dispersed EXAFS, Debye-Scherrer rings, or Laue diffraction patterns on time scales of less than a microsecond is now feasible. When it is appreciated that microinsertion devices planned for present storage rings and for machines being considered for the millennium will offer even greater intensities and brilliances, it is obvious that synchrotron sources will be quite indispensable in the future to those concerned with elucidating the mode of operation of inorganic catalysts under working conditions.

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