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New methods of probing the structure of catalysts

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Some of the methods used in probing the structure and performance of heterogeneous catalysts are discussed. We consider X-ray diffraction, neutron diffraction and neutron inelastic scattering, high-resolution electron microscopy, electron diffraction, electron energy loss spectroscopy, and computational methods. The determination by X-ray diffraction of siting and occupancy of extra-framework cation Ni^{2+} in faujasite or by neutron diffraction of H^+ in La^{3+} -Y catalyst are discussed. Some of the methods are complementary and a combination of two or more can be used to gain a better understanding of the problem.

1. Introduction

Of the techniques available for the characterization of solid catalysts, only a few are applicable under *in situ* conditions. From the tabulation below we see that many of the powerful methods that are capable of disclosing so much about the nature of a catalyst in the *ex situ* state are inapplicable for *in situ* studies. For example, all those techniques that entail deployment of either primary or liberated electrons to probe the properties of surfaces disqualify themselves for use when gas pressures are such as to render electron mean-free-paths infinitesimal. Nevertheless, such methods along with others that are not usable when ambient conditions are severe, do have a validity of their own, and can still illumine our knowledge of catalysts. Electron-energy-loss spectroscopy, both the high-resolution-low-energy and low-resolution-high-energy varieties, are valuable in this regard. Likewise electron microscopy, solid-state NMR and other techniques outlined later, afford useful insights into the structure and performance of heterogeneous catalysts.

Here we focus upon the merits and potential of some of the more powerful methods of characterization by reference to certain specific problems central to the concerns of those seeking to understand more about the nature and behaviour of heterogeneous catalysts. Particular emphasis is placed here on *uniform heterogeneous catalysts*, i.e. those that are monophasic and have their active sites distributed in a spatially uniform fashion throughout their accessible bulk. Zeolites and certain oxides are in this category.

2. X-ray diffraction

With the aid of powder X-ray diffractometry, it is readily possible to monitor the key structural and compositional changes accompanying the production of active or poisoned catalysts and, with the ever-expanding and retrievable library of X-ray diffractograms, identification of crystalline phases becomes progressively easier. Moreover, with appropriate reactors, fitted with beryllium windows for example, it is possible to track the formation of many hitherto unsuspected crystalline and non-crystalline phases in very well-known catalysts, such as the reduced iron oxide used in

Table 1.

Methods based on beams of either primary scattered or liberated electrons	LEED, AES, XPS, UPS, HREM, ED, EELS, inverse photoemission or X-ray emission
Particles in→particles out	Neutron elastic and inelastic scattering (Rietveld), PIXE
Photons in→photons out	IR, Laser-Raman, X-ray absorption (EXAFS, XANES, NEXAFS) Rietveld X-ray powder profile
Magnetic resonance and related techniques	

the synthesis of ammonia (Rayment *et al.* 1985). Suitably constructed cells can also enable us to probe the siting of reactants sorbed at low temperatures into zeolitic catalysts using X-ray diffraction. We demonstrated (Gameson *et al.* 1986) that the location of a model reactant, namely xenon, with a protonated zeolite could be pinpointed by X-ray diffraction over the temperature range from 10 to 220 K. More recently, using CH_3Cl as a reactant—known to be capable of conversion to aromatic hydrocarbons on zeolitic catalysts—we have used the same technique employing the same model catalyst, the H^+ -form of zeolite rho.

One of the principal advantages of the X-ray technique is that it can be used—in the Rietveld method of refinement of powder profiles—to follow the course of significant, if subtle, structural changes that take place at high-temperature under actual *in situ* reactor conditions. Thus, the sitings and occupancies of extra-framework cationic nickel, potassium and sodium in typical faujasitic zeolites at temperatures in the range 400° to 500°C have been determined (Thomas *et al.* 1988).

Transition-metal exchanged zeolites, both in their unreduced and reduced form, are powerful catalysts for a wide range of organic reactions, including selective oxidation, hydrogenation and isomerization. The precise nature of the catalytic activity, selectivity and stability are, however, critically dependent upon the pretreatment, especially the thermal history, to which the metal-exchanged zeolite is subjected. Nickel-containing zeolites show catalytic activity for methanation, hydrogenation and dehydrogenation. In addition, nickel in the cationic form is a potential catalyst for hydrocarbon transformation: on dehydration, cationic nickel interacts with the framework oxygens but it can also possess free coordination sites for interaction with reactants. The catalytic performance of such zeolites is governed by the location of the extra-framework ions in the intrazeolitic cavities and upon their coordination to the framework. The sitings of Ni^{2+} and other ions were found to be different from those previously reported for the catalyst at room temperature. There were also significant differences in the location of cations and in the reducibility of Ni^{2+} depending upon the nature of the treatment (e.g. steam treatment or washing with alkaline solutions) to which the original zeolite is subjected prior to dehydration and/or reduction (see figure 1).

More specific uses can be made of *in situ* Rietveld analysis of zeolitic catalysts. Such approaches should, in association with other *in situ* X-ray procedures, such as those of Gallezot (1984) who have retrieved radial distribution functions for metal-loaded zeolite, be of considerable value in future studies of 'live' catalysts.

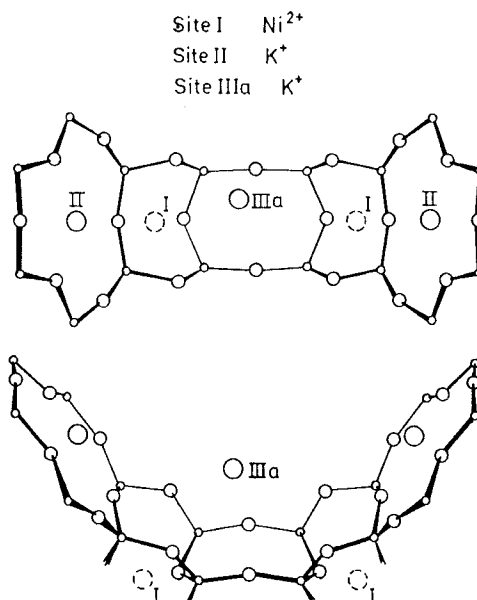


Figure 1. From a Rietveld analysis of powder X-ray diffractograms recorded at high temperature, the migration of cations (typically, Ni²⁺, K⁺ and Na⁺) between the various extra-framework sites of a zeolite can be evaluated, e.g. the location of Ni²⁺ and K⁺ cations at 450°C in zeolite Y, shown here.

3. Neutron diffraction and neutron inelastic scattering

Given adequate neutron fluxes, the prospects for *in situ* characterization here are even brighter than those pertaining to X-rays. To date, however, Rietveld analysis of powder neutron-diffractometry has been more conveniently carried out on catalysts studied at low temperatures (Wright *et al.* 1986). The sitings of typical reactant and product species in a number of viable zeolitic catalysts have been determined. Thus, benzene—which is one of the products of catalytic conversion of *n*-hexane in suitably modified K⁺-exchanged zeolite L—tends to take up a position in which the molecular caps a K⁺ ion, or one in which the plane of the molecule is sandwiched between two K⁺ ions either side of the plane.

A valuable insight provided by Rietveld profile analysis of neutron-diffraction data is the atomic detail of the active site in La³⁺-exchanged zeolite Y catalysts (Eddy *et al.* 1984). The specific location of the detachable proton loosely bound to a framework oxygen atom at the active site in La³⁺-Y catalysts offers direct experimental evidence for the postulated mode of action of Bronsted acidic zeolitic catalysts, as well as the reality of cation hydrolysis (figure 2).

With the recent improved resolution of neutron diffractometers and the demonstrated ability to cope, *ab initio*, with the determination of hitherto unsolved structures (Attfield *et al.* 1986) one may soon expect more advances in this approach to the characterization of catalysts.

Neutron inelastic scattering is already proven as a viable technique for *in situ* studies of hydrodesulphurization catalysts. Scattering by interlamellar and layer-bound hydrogens in MoS₂ catalysts has been reported by Vasudevan *et al.* (1982). It has recently been applied to model zeolites containing enclatherated organic cations.

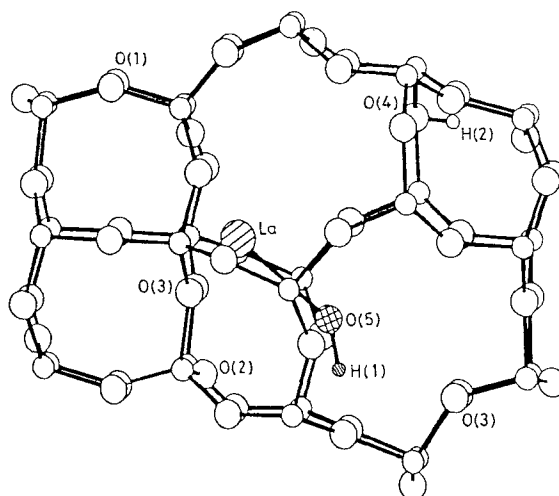


Figure 2. The truncated octahedral element in zeolite La-Y, showing one of the hexagonal prismatic linkages to the adjacent element. Site SI', here shown occupied by La is in the hexagonal window.

4. High-resolution electron microscopy (HREM), electron diffraction (ED) and electron-energy loss spectroscopy (EELS)

A modern high-resolution electron microscope to which has been attached an electron spectrometer and a detector for X-ray emission can yield the following information for materials ranging upwards in mass from *ca* 10^{-19} g and in volume from 10^{-18} cm³:

- (a) the crystallographic phase, and its space group, from ED patterns;
- (b) the elemental composition from X-ray emission and EELS;
- (c) the projected image and, in favourable circumstances, the crystal structure, from HREM; and
- (d) the valence state, and coordination of specific (especially light) atoms from EELS.

We summarize below some specific results.

4.1. Determination of the structure of ZSM-23

Here, electron diffraction played a crucial role (see Wright *et al.* 1985). From the space group and unit cell dimensions, retrievable from ED, plausible models of the unit cell could be formulated. By invoking evidence from ²⁹Si MASNMR (Thomas and Klinowski 1985) and other key items of information, it was possible to arrive at a specific, trial structure which could then be refined using X-ray powder diffractometry combined with Rietveld analysis as in section 1 above.

4.2. Selective oxidation oxide catalysts

A hitherto unknown structure, continuing crystallographic shear and regular layering of mixed-oxide sheets, for the catalyst Bi₂(Mo, W)₁₂O₃₅ known to be effective in converting propylene to acrolein, was determined by a combination of high-resolution imaging and computer simulation of images (Thomas *et al.* 1985).

4.3. New structural inter-relationships in mixed oxide catalysts

The extensive family of bismuth molybdates ($m\text{Bi}_2\text{O}_3 \cdot n\text{MoO}_3$) turn out to be almost exclusively based on the fluorite structure (Buttrey *et al.* 1986). In effect, the seemingly complex structures found in this series (variable m/n), as well as the analogous $m\text{Bi}_2\text{O}_3 \cdot n\text{Nb}_2\text{O}_5$, $m\text{Bi}_2\text{O}_3 \cdot n\text{V}_2\text{O}_5$ etc., systems are all essentially superstructures of the defect fluorite form (i.e. the δ -form) of Bi_2O_3 (Zhou *et al.* 1986). This fact has interesting repercussions so far as designing new, conventional and new photocatalysts is concerned (Zhou *et al.* 1987).

4.4. Valence states of transition metals and the coordination of light elements in oxide catalysts

The ratio of the intensities of L_2/L_3 lines are good pointers to the number of electrons in the valence shell of a transition metal (Williams *et al.* 1987, Thomas *et al.* 1985). Moreover, it has been shown that in favourable circumstances this ratio can be conveniently recorded using combined electron-energy-loss spectroscopy and electron microscopy so that high spatial resolutions are feasible. Catalyst particles of less than 10 \AA in linear dimension can be studied in this way.

In association with Professor E. Zeitler and his associates, we have, with the aid of parallel detection techniques, demonstrated the great promise of EELS in probing the environment of light elements (Brydson *et al.*, submitted and in preparation). Thus, there is no difficulty in distinguishing tetrahedral from octahedral aluminium ion in an oxide environment (see figure 3). Likewise environments for boron, beryllium and oxygen appear to be resolvable using this technique, which has exceptional spatial resolution. Effectively we use electron energy loss near edge structures (ELNES)—the analogue of XANES and NEXAFS—for such work.

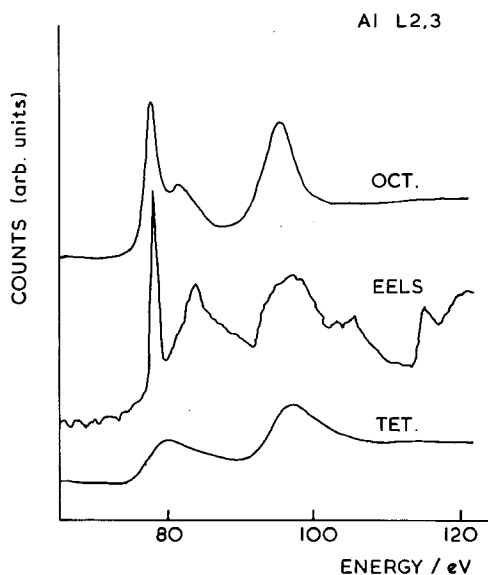


Figure 3. Electron energy loss spectrum (labelled EELS) of a microscopic specimen of a mineral (rhodizite) which is known to contain octahedrally coordinated Al. Top and bottom curves are calculated spectra.

5. The microstructure of colloidal catalysts

HREM, combined with X-ray emission, and optical and electron diffraction are powerful means of identifying those colloidal systems where the degree of translational order within the particles is high from those where it is low. Both metallic and oxidic colloids have been studied (Jefferson *et al.* 1986, Tirado *et al.* 1987, Harriman *et al.* 1987). Promising progress has recently been achieved in correlating the microstructure of these colloids with their performance as catalysts. For example, it transpires that colloids of Ir are crystalline, whereas those of $\text{IrO}_2 \cdot x\text{H}_2\text{O}$ are amorphous and slowly aggregate, even when protected with a surface layer of polymer. Reduction of $\text{IrO}_2 \cdot x\text{H}_2\text{O}$ produces Ir which, in turn, is oxidizable to $\text{IrO}_2 \cdot x\text{H}_2\text{O}$ under mild conditions. Colloids of $\text{IrO}_2 \cdot x\text{H}_2\text{O}$ catalyse the oxidation of water to O_2 , but the efficiency is modest. Colloidal Ir, however, is a good catalyst for reduction of water to H_2 , for the hydrogenation of unsaturated groups and for dissociation of formic acid and hydrogen peroxide.

6. Computational procedures

It is possible nowadays to ascertain what changes in the local density of electronic states are wrought locally at specific surface sites in metal surfaces brought about by the presence of poisons or promoters. It is also possible to glean information concerning the siting, energetics and mobility of reactant species located within the internal pores of certain catalysts from the potential energy distribution functions evaluated by Monte Carlo methods (Nicholson and Parsonage 1982). Yashonath *et al.* (1988), building upon earlier pioneering studies by Kiselev and Du (1981), have recently undertaken a computational study of how reactant hydrocarbons are bound within the cages and migrate along the inner walls of zeolite catalysts. To date, they have examined only the case of methane in a zeolite Y host. Promising results have emerged, which yield information about the range and distribution of binding sites in such systems at relatively low temperatures. In this way, for any given set of conditions appropriate for a monophasic, uniform zeolitic catalyst, e.g. a particular value of Si/Al ratio for a particular combination of two or more exchangeable cations distributed in a prescribed fashion along available sites, we may infer how tenaciously held or mobile a reactant is likely to be at a specific temperature.

In conclusion, we note that a substantial number of powerful new approaches can be adopted for the study of solid catalysts. Some of these approaches promise to uncover features not hitherto accessible using conventional techniques.

References

- ATTFIELD, J. P., SLEIGHT, A. W., and CHEETHAM, A. K., 1986, *Nature, Lond.*, **322**, 620.
BRYDSON, R. D., ZEITLER, E., ERGLER, W., THOMAS, J. M., WILLIAMS, B. G., LUIDUER, T., SAUER, H., and SCHLOGL, R. (submitted).
BRYDSON, R. D., VVEDENSKY, V., ENGEL, W., WILLIAMS, B. G., ZEITLER, E., and SAUER, H., 1988, *J. phys. Chem.* (in the press).
BUTTREY, D. J., JEFFERSON, D. A., and THOMAS, J. M., 1986, *Phil. Mag.*, **73**, 897.
EDDY, M. M., CHEETHAM, A. K., and THOMAS, J. M., 1984, *J. chem. Soc. chem. Comm.*, 1337.
GALLEZOT, P., 1984, *Catalysis, Science and Technology*, **5**, 221.
GAMESON, I., WRIGHT, P. A., RAYMENT, T., and THOMAS, J. M., 1986, *Chem. Phys. Lett.*, **123**, 145.
HARRIMAN, A., THOMAS, J. M., and MILLWARD, G. R., 1987, *Nouv. J. Chem.* (in the press).
JEFFERSON, D. A., THOMAS, J. M., MILLWARD, G. R., HARRIMAN, A., and BRYDSON, R. D., 1986, *Nature*, **323**, 428.
KISELEV, A. V., and DU, P. Q., 1981, *J. chem. Soc. Faraday Trans. II*, **17**, 17.

- NICHOLSON, D., and PARSONAGE, N. G., 1982, *Computer Simulation and the Statistical Mechanics of Adsorption* (New York: Academic Press).
- RAYMENT, T., SCHLOGL, R., THOMAS, J. M., and ERTL, G., 1985, *Nature*, **315**, 311.
- THOMAS, J. M., WILLIAMS, C., and RAYMENT, T., 1988, *J. chem. Soc. Faraday Trans. I* (in the press).
- THOMAS, J. M., and KLINOWSKI, J., 1985, *Adv. Catalysis*, **33**, 199.
- THOMAS, J. M., JEFFERSON, D. A., and MILLWARD, G. R., 1985, *JEOL News*, **23E**, 7.
- THOMAS, J. M., WILLIAMS, B. G., and SPARROW, T. G., 1985, *Accnts. chem. Res.*, **18**, 324.
- TIRADO, J. M., THOMAS, J. M., MILLWARD, G. R., JEFFERSON, D. A., and CHARLES, S. W., 1987, *J. chem. Soc. chem. Comm.*, 365.
- VASUDEVAN, S., THOMAS, J. M., and WRIGHT, C. J., 1982, *Bull. Soc. Chem. Belg.*, **90**, 1215.
- WILLIAMS, B. G., THOMAS, J. M., SPARROW, T. G., and RAO, C. N. R., 1987, *J. phys. Chem.*, **88**, 5769.
- WRIGHT, P. A., THOMAS, J. M., MILLWARD, G. R., BARRI, S. A. I., and RAMDAS, S., 1985, *J. chem. Soc. chem. Comm.*, 1117.
- WRIGHT, P. A., NOWAK, A. K., THOMAS, J. M., and CHEETHAM, A. K., 1986, *Nature*, **318**, 611.
- YASHONATH, S., THOMAS, J. M., NOWAK, A. K., and CHEETHAM, A. K., 1988, *Nature, Lond.*, **331**, 601.
- ZHOU, W., JEFFERSON, D. A., and THOMAS, J. M., 1986, *Proc. Roy. Soc.*, **A406**, 173.
- ZHOU, W., THOMAS, J. M., JEFFERSON, D. A., and ALARIO FRANCO, M., 1987, *J. phys. Chem.*, **91**, 512.