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Probing Active Sites in Solid Catalysts for the Liquid-phase Epoxidation of Alkenes

Gopinathan Sankar,[a] Fernando Rey,[a] John Meurig Thomas,*[a] G. Neville Greaves,[a,b] Avelino Corma,[c] Barry R. Dobson[b] and Andrew J. Dent[b]

[a] Davy Faraday Research Laboratory, The Royal Institution of GB, 21 Albemarle Street, London, UK W1X 4BS
[b] The EPSRC Daresbury Laboratory, Daresbury, Warrington, Cheshire, UK WA4 4AD
[c] Instituto de Tecnologia Quimica, Universidad Politecnica de Valencia, Camino de Vera s/n, 46071 Valencia, Spain

Using X-ray absorption fine structure measurements with a synchrotron source, the local environment of the titanium-centred active site of a siliceous mesoporous catalyst for the epoxidation of cyclohexene by H_2O_2 has been determined prior to the onset and during the course of catalysis.

More so perhaps than any other probe, with the possible exception of neutron scattering, confocal laser microscopy and sum-frequency generation, synchrotron radiation offers a definitive means for determining the environment of active sites in solid catalysts under operating conditions. There are many ways in which this determination may be effected. First, using Rietveld X-ray powder profile refinement:[1] in this way the precise movement and location of Ni^{2+} ions in a Ni–Na zeolite Y catalyst as it is converted in the presence of reactant (acetylene) from an inactive precursor state to an active catalyst for cyclotrimerization[2] (to benzene), may be followed, *in situ*, by accumulating a series of high-resolution diffractograms. Second, *via* energy-dispersive X-ray diffractometry,[3] where, for example, there is a fixed-geometry environmental cell and a germanium detector beyond the synchrotron beam: in this way the entire powder diffraction pattern of the catalyst may be continuously monitored during the course of its activation, operation, decline and (if appropriate) regeneration. (Catalytic natural gas conversion by CO_2 using a series of pyrochlore has been investigated[4] in this fashion at temperatures up to 615 K). Third, energy-dispersive X-ray absorption spectroscopy[5] (EDEXAFS): this has been used to follow the dynamics of dehydration and activation of transition-metal-ion exchanged zeolites and also to determine the surface area of supported copper catalysts.[6] Last, and most important, combined *in situ* X-ray diffraction[7–9] and X-ray absorption (XANES and EXAFS) is feasible with synchrotron sources, and it yields[10] simultaneous changes in bond lengths and oxidation state of the active centre in a solid inorganic catalyst during calcination and reduction.

There has long been a pressing need for comparable *in situ* studies to be carried out on the elucidation of active sites in solids that catalyse liquid-state reactions. To examine the feasibility of doing so we have chosen a system of considerable significance in petrochemical and pharmaceutical contexts: the epoxidation of alkenes by H_2O_2 catalysed by Ti^{IV} ions embedded in porous solids.[11–13] In particular, we have prepared a Ti-incorporated mesoporous silica belonging to the so-called MCM-41 family,[14] recently reported, and followed changes in the pre-, near- and extended-edge structures[15] of the titanium K-absorption edge both prior to and during the course of catalysis. The spectra were recorded (as fluorescence emission, see refs. 8 and 16) using a special cell, to be described fully elsewhere, in which the ultraporous catalyst is in intimate contact with the flowing liquid reactants in a space (*ca.* 100 μm) separated by Kapton windows (25 μm thick).

The X-ray absorption near edge spectra of the as-prepared (template-incarcerated) Ti-incorporated mesoporous silica analogue (Si/Ti = 60 : 1), of the calcined (in O_2 at 550 °C for 2 h) as well as of the catalyst (100 mg) in its active state for conversion of cyclohexene (10 ml) to the epoxide {in the presence of H_2O_2 [0.8 g of a H_2O_2–H_2O (65/35) mixture] and methanol (25 ml) as solvent}, are shown in Fig. 1 (see also Table 1). The pre-edge peak intensity is known to be sensitive to the coordination[17] thus serving as a fingerprint in assessing the local environment around titanium. The Fourier transforms of the Ti K-edge EXAFS along with the best fit obtained for the first near neighbours are shown in Fig. 2. The decrease

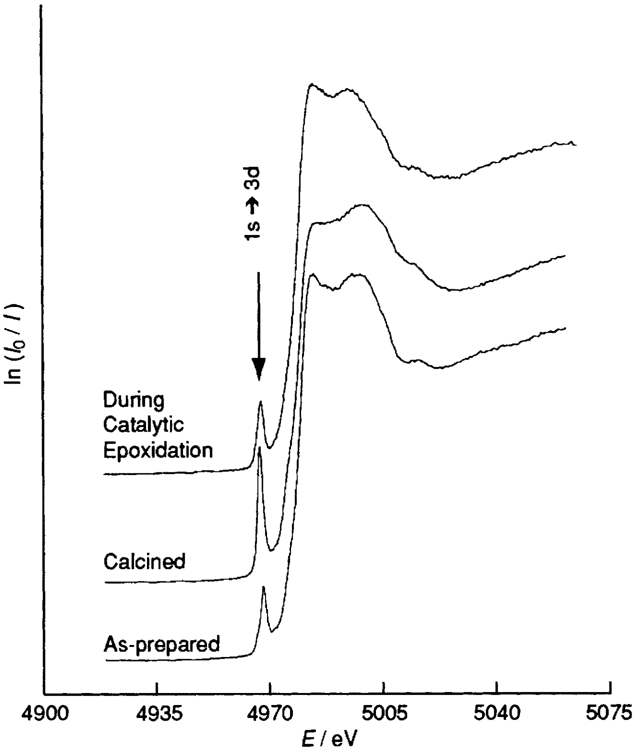

Fig. 1 Normalised Ti K-edge XANES spectra of titanium-incorporated MCM-41 catalyst. The pre-edge peak and intensities referred to in the text are denoted by the 1s→3d transition.

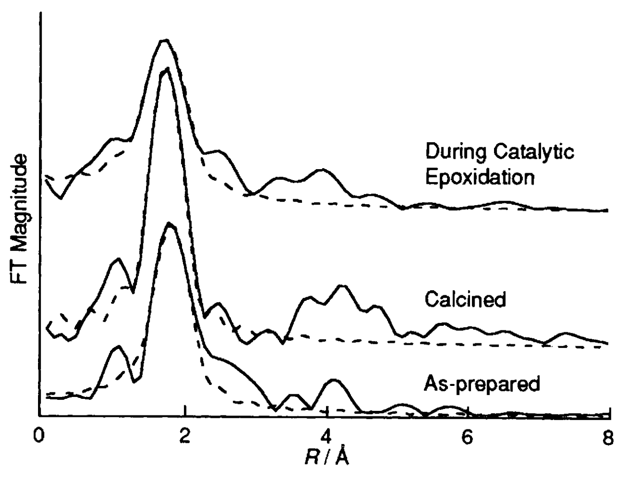

Fig. 2 Fourier transform of the Ti K-edge EXAFS of the titanium-incorporated MCM-41 catalyst. The solid line shows the experimental data, and the dashed one the Fourier transform of the calculated EXAFS obtained from the best fit using a least-squares procedure.

Table 1 Summary of results of Ti K-edge XANES and EXAFS spectra

	Pre-edge intensity[a]	Ti–O distance/Å[b]	Ti–O coordination number[b]	$2\sigma^2$/Å^2[b]
As-prepared	0.22	1.87	4.5	0.0190
Calcined	0.49	1.80	3.7	0.0098
During catalytic epoxidation	0.23	1.82	4.6	0.0250

[a] Intensity of the peak in arbitrary units (Fig. 1). [b] The error involved in the determination of Ti–O distance is ±0.02 and 10% in the coordination number.

in Ti–O distances upon calcination from 1.87 Å (for the as-prepared material) to 1.80 Å, evident in Fig. 2, is consistent with the generation of a well-ordered tetrahedral environment around titanium and also with the increase in the pre-edge intensity. These changes arise from the removal of the template on calcination. During reaction the titanium environment again alters, with an increase in disorder reflected in the pre-edge feature which falls in intensity. The Ti–O distance, however, stays close to the tetrahedral value of 1.80 Å. The increase in disorder is the result of participation of titanium in the catalytic conversion of cyclohexene to the corresponding epoxide in the presence of H_2O_2. Analysis of the various Ti geometries from fitting the background-subtracted EXAFS spectra yields the information summarized in Table 1. Detailed discussion of this structural modifications around titanium will be reported elsewhere.

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