

# Energy filtered transmission electron microscopy (EFTEM) in the characterization of supported TiO<sub>2</sub> photocatalysts

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## Energy filtered transmission electron microscopy demonstrates whether TiO<sub>2</sub> is on the surface or enters the pore channel system of zeolites.

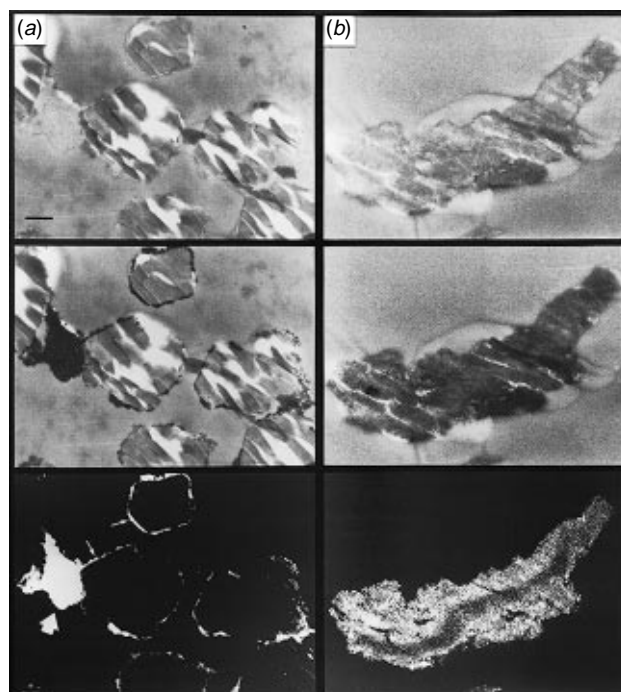
The widely studied photocatalyst, TiO<sub>2</sub>, is often supported, either to simplify material handling or to modify the properties of the catalyst. Our group<sup>1,2</sup> and others<sup>3</sup> have exploited silica and zeolite supports. Our intention has been to modify the catalytic behaviour of the systems through convolution of the very general, non-selective, photocatalytic oxidation activity of TiO<sub>2</sub> with the absorption characteristics and specific oxidative catalysis available with high silica zeolites. In order to understand and manipulate such systems, it is necessary to develop tools for the detailed examination of the distribution of TiO<sub>2</sub> on and in the supports. In our earlier papers,<sup>1,2</sup> we described the information derivable from scanning electron microscopy, powder X-ray diffraction and vibrational spectroscopy. These indicated that TiO<sub>2</sub> thin films or microparticles on the zeolites were the most photoactive. In the case of large silica particles which could be examined in the cross-section, it was possible to gain insight into the behaviour of photocatalytic sites in the interior of the particles.<sup>2</sup> However, a severe limitation was the inability to image the distribution of TiO<sub>2</sub> in conventional small zeolite particles.

This communication describes a technique for imaging such a distribution. It exploits energy filtered transmission electron microscopy (EFTEM) (which has been used for mapping other elements<sup>4-6</sup>) to image cross-sections of micron-sized zeolite particles with varying sizes of mesopores which favour different distributions of TiO<sub>2</sub>. The basis of the technique is that energy losses of electrons that pass through a sample are characteristic of the chemical elements present. Electrons are separated according to energy loss by a spectrometer which also acts as a lens.<sup>7</sup> The Ti-specific ionization edge L<sub>2,3</sub> occurs at 456 eV. Consequently, a 430 eV image does not contain any Ti-specific information, whereas a 460 eV image is 'Ti-enhanced'. A net Ti distribution can be determined by subtracting the pre-edge reference image from the post-edge Ti-enhanced image. Samples were imbedded in QUETOL and thin-sectioned with an ultramicrotome to sections 30 nm thick. Energy loss micrographs were recorded with a Zeiss EM902 instrument equipped with an imaging spectrometer. A 500 μm condenser aperture, a 60 μm objective aperture and a 20 eV energy selecting slit aperture were used. Images were recorded at a magnification of 13 000 × on SO-163 electron image film (Kodak). The film was then digitized and analysed as described previously.<sup>7</sup>

We report here on the contrast of a demonstration sample pair that illustrates the power of the technique. Our preferred method<sup>1</sup> for TiO<sub>2</sub> loading of zeolites is to stir a colloid of TiO<sub>2</sub> with zeolite, remove the solvent and calcine at a moderate temperature (450 °C). Some experiments have suggested that the TiO<sub>2</sub> colloids may be labile so that smaller particles in equilibrium with the dominant ones might enter pores of the support which are smaller than the nominal particle size in the colloid, leading to distribution of TiO<sub>2</sub> into the particle interior. To test this, we have studied the loading of 'Q-sized' TiO<sub>2</sub>

particles with diameters of 20–40 Å<sup>8</sup> into two compositionally similar zeolites of the mesoporous MCM-41 family,<sup>9</sup> one of which had an average pore diameter of 20 Å (MCM-20), the other with an average pore diameter of 60 Å (with pores up to 120 Å) (MCM-60). The pore size distributions of these two were measured by N<sub>2</sub> absorption in an ASDI RXM-100 catalyst characterization system. Penetration of Q-sized particles into the larger pore-sized MCM-41 should be facile. In contrast, penetration into the smaller pore size (20 Å) requires that the Q-sized colloid is in labile equilibrium with fragments smaller than the nominal particle size.

In Fig. 1, we show the net images (lower) resulting from the subtraction of the pre-edge reference image (upper) from the post-edge Ti-enhanced image (middle). The MCM-60 is shown in Fig. 1(b) and images of MCM-20 are shown in Fig. 1(a). These two images are representative of a number we recorded, and it must be understood that we do not control the orientation of the particles with respect to cutting direction of the ultramicrotome. A dark region across the centre of the particle shown in Fig. 1(b) (lower) indicates that TiO<sub>2</sub> particles did not fully penetrate the zeolite but the distribution of light dots clearly reveals deep penetration of TiO<sub>2</sub>. In Fig. 1(a), we see that little penetration of TiO<sub>2</sub> into MCM-20 particles occurs.



**Fig. 1** Energy filtered images of zeolites MCM-41 with average pore diameters of 20 Å (a) and 60 Å (b). Pre-edge images were recorded at 430 eV (upper panels), post Ti-edge images were recorded at 460 eV (middle panels). The lower panels show the net images after alignment, subtraction and inversion of contrast (Ti-rich regions shown as white on black background). Scale bar = 210 nm.

The hint that labile equilibration of the colloid particles with smaller TiO<sub>2</sub> polycations occurs is refuted. Where the colloid is prepared at particle sizes greater than the pore size, penetration is unimportant. Fig. 1(a) also shows that not all of the TiO<sub>2</sub> has been distributed in a uniform thin layer over the zeolite (small arrows, lower), but that aggregates of TiO<sub>2</sub> can form (large arrow, lower). The spatial detail in these images approaches the resolution limits of the electron microscope at 13 000 × magnification. Structure in the maps, therefore, is better resolved by about two orders of magnitude than can be obtained with X-ray microanalysis in the scanning electron microscope.

We thank the National Sciences and Engineering Research Council of Canada for support.

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*Received, 8th August 1996; Com. 6/05530C*