

Photoreactivity of ETS-10

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Irradiation of H-ETS-10 in the presence of adsorbed methanol or ethene causes photoreduction of Ti(IV) to Ti(III); photoreduction does not occur for Na, K-ETS-10, but a photoinduced polymerization of ethene is observed.

ETS-10 is a titanosilicate zeolite with a novel structure comprising one-dimensional chains of corner-linked TiO_6 octahedra surrounded by tetrahedral silicate units, generating a three-dimensional 12-ring pore system.¹ There is particular interest in the O–Ti–O–Ti–O chains, which have been described as semiconductor nanowires within an insulating sheath.² Titanium in ETS-10 can be chemically reduced by adsorbing sodium vapour into ETS-10,³ suggesting that electronic communication can occur between the semiconductor chains and species in the pores. There is also an early report of photocatalytic activity of ETS-10 in the oxidation of organic alcohols,⁴ which likewise implies that electron transfer can occur through the silicate ‘insulation’. The photoreactivity of conventional anatase photocatalysts has been extensively studied; band gap irradiation of anatase in the presence of adsorbed organic compounds causes photoreduction of Ti(IV) to Ti(III), due to trapping of holes by the adsorbed organic and consequent trapping of electrons at Ti(IV) sites.⁵ We have begun a study comparing the photoreactivity of anatase with that of ETS-10, and report here that the photoreduction of ETS-10 depends on the presence of defects in the structure.

Two ETS-10 samples were studied: a hydrogen exchanged material provided by Engelhard,⁶ and a sample synthesized in-house following established procedures⁷ which contains sodium and potassium as the charge balancing cations. Both samples gave X-ray powder diffraction patterns characteristic of ETS-10;¹ the higher angle peaks of the H-ETS-10 sample were however substantially broadened relative to Na,K-ETS-10, indicating a higher degree of disorder in the proton exchanged sample (chemical analysis of this sample showed the extent of proton exchange to be $\text{H}/(\text{H} + \text{Na} + \text{K}) = 0.78$). SEM showed average crystallite sizes to be around 2 μm for Na,K-ETS-10, but 0.3 μm for H-ETS-10. Indications of greater disorder in the O–Ti–O–Ti–O chains in the proton exchanged material came from the absence of the intense Raman band at 732 cm^{-1} attributed to Ti–O stretching vibrations in the chains⁸ which is present in the Na,K-ETS-10, and substantially increased Debye–Waller factors in the Ti K-edge EXAFS of H-ETS-10 compared with Na,K-ETS-10.⁹ ^{29}Si NMR spectra of the H-ETS-10 were similar to those previously reported,⁶ showing retention of Si–O–Ti bonds. A commercial (Degussa P25) anatase sample was used for comparison with ETS-10.

Photoreduction experiments were performed in a vacuum EPR cell; samples were outgassed *in vacuo* at 573 K, then exposed to either methanol or ethene vapour and irradiated at room temperature with a 125 W mercury arc lamp. Irradiation of anatase in the presence of methanol or ethene produces a dark blue colour and an intense broad EPR signal of Ti(III), with parameters $g_{\perp} = 1.973$, $g_{\parallel} = 1.949$ (measured at 77 K). This signal could not be detected at room temperature. Similar signals have been previously attributed to Ti(III) cations on lattice sites distributed through the bulk of anatase, or to surface Ti(III) cations, in both cases with distorted octahedral coordination.¹⁰ The Ti(III) signal was removed when the sample was

evacuated then exposed to oxygen, but no new signals were formed.

Fig. 1 shows EPR signals recorded at room temperature following irradiation of H-ETS-10 in the presence of ethene. The sample turns grey and the new signal which appears is shifted significantly to higher field relative to that obtained with anatase ($g_{\text{av}} \approx 1.95$). The other important difference from anatase is that this signal could be observed at room temperature. Subsequent exposure to oxygen (5 Torr) gave weak new signals in the vicinity of $g = 2.010$, but evacuation followed by exposure to 5 Torr of oxygen totally removed the Ti(III) signal (and the grey colour) and enhanced the new signals [Fig. 1(c)]. Closer examination of the new signals reveals that one component is the superoxide ion O_2^- adsorbed on Ti(IV) sites ($g_{zz} = 2.022$, $g_{yy} = 2.011$, $g_{xx} = 2.004$).¹¹ Identification of the other species is less certain, but the lower field shoulders may be the g_{zz} components of superoxide species adsorbed on sites of lower formal charge.¹² Similar spectra were obtained when H-ETS-10 was irradiated in the presence of adsorbed methanol and subsequently exposed to oxygen.

The Ti(III) signal formed on irradiation of H-ETS-10 in the presence of the adsorbed ethene or methanol differs from that formed in anatase under the same conditions. This is not unexpected if the Ti(III) is in a one-dimensional O–Ti–O–Ti–O chain rather than the three-dimensional anatase lattice. However it is clear from the reactivity of this species towards oxygen, and in particular from the observation of O_2^- adsorbed on Ti(IV)

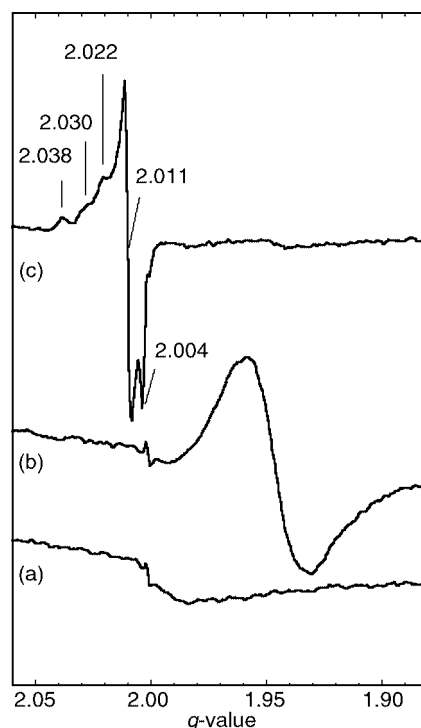


Fig. 1 EPR signals from H-ETS-10: (a), exposed to ethene prior to irradiation; (b), irradiated for 2 h; (c), evacuated at room temperature then exposed to 5 Torr of oxygen.

sites, that H-ETS-10 contains exposed titanium sites which should not be present in a defect free ETS-10 structure.

This conclusion is supported by the observation that when the same experiments were conducted with Na,K-ETS-10 in which the spectroscopic evidence indicates that the O–Ti–O–Ti–O chains are relatively defect free, no photoreduction was observed; *i.e.* no colour changes occurred on irradiation in the presence of methanol or ethene, and no Ti(III) signals were detected by EPR.

Nevertheless, *in situ* FTIR studies of Na,K-ETS-10 in the presence of adsorbed ethene show that a photoinduced reaction of ethene with the ETS-10 does occur. Fig. 2 shows IR spectra recorded in an *in situ* cell of Na,K-ETS-10 following adsorption of ethene and subsequent irradiation (these are difference spectra from which the spectrum of the dehydrated ETS-10 prior to admission of ethene has been subtracted, and ratioed against a background containing the gas phase ethene to remove gas phase contributions to the spectra).

On irradiation bands due to adsorbed ethene (*e.g.* 3083, 1613, 1445 and 1338 cm^{-1}) are reduced in intensity, and new bands appear and grow in the $\nu(\text{OH})$ region (3660, 3580 cm^{-1}), in the $\nu(\text{CH})$ region (2926 and 2856 cm^{-1}), at 1632 cm^{-1} and at 1468 cm^{-1} . Evacuation at room temperature removes the adsorbed ethene bands but leaves the new bands unchanged.

The bands appearing at 2926, 2856 and 1468 cm^{-1} are characteristic of saturated CH_2 groups,¹³ suggesting that polymerization of ethene has occurred to form $(\text{CH}_2)_n$ chains. On the other hand, the bands at 3660, 3580 and 1632 cm^{-1} are close to those expected for isolated (non-hydrogen bonded) water

molecules.¹⁴ This experiment thus suggests that in Na,K-ETS-10 holes and electrons formed on irradiation both react with adsorbed ethene. A free radical polymerization of ethene may be initiated by electrons generated in the O–Ti–O–Ti–O chains, while the formation of adsorbed water may occur as a result of oxidation of adsorbed ethene by positive holes (involving reaction of lattice oxide ions). The sharpness of the bands due to adsorbed water indicates that these are isolated water molecules. It is important to note also that no reaction occurred in the absence of irradiation.

This chemistry is different from that occurring in H-ETS-10, where electron trapping occurs preferentially at Ti(IV) sites associated with defects. An IR experiment similar to that described above was performed on ethene adsorbed in H-ETS-10. In this case irradiation caused a similar reduction in intensity of the bands due to physisorbed ethene, but the only new bands appearing were broad bands due to hydrogen bonded adsorbed water, at *ca.* 3300 and 1630 cm^{-1} . In particular, no new bands due to polyethene were detected in H-ETS-10.

Further work is needed to establish details of the photoreduction and photoinduced polymerization mechanisms. Further characterization of the defect sites in H-ETS-10 is also in progress. It is clear however that the defect sites are important in the photoreactivity of these novel materials. Our observation of photoinduced ethene polymerization in Na,K-ETS-10 also confirms that electron transfer can occur between the semiconductor chains and molecules adsorbed in the ETS-10 pores. This has important consequences for the potential use of ETS-10 as a photocatalyst.

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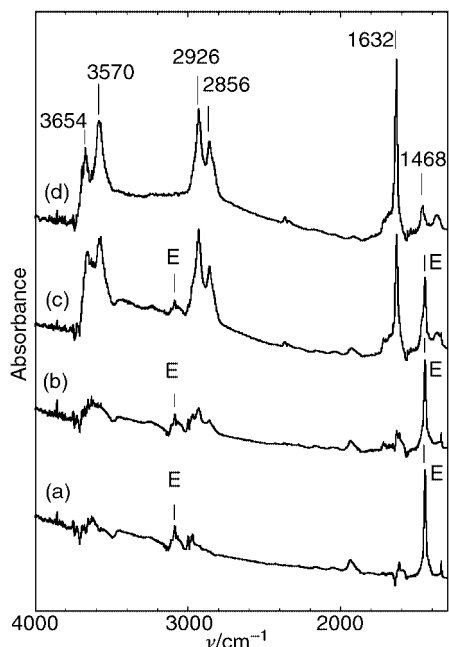


Fig. 2 *In situ* FTIR spectra of ethene in Na,K-ETS-10 (gas phase and background spectrum of ETS-10 subtracted): (a) exposed to ethene (70 Torr) at room temperature; (b), irradiated 90 min; (c), irradiated 300 min; (d), evacuated at room temperature. (E denotes bands due to physisorbed ethene).