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STUDY OF THE STRUCTURE AND PROPERTIES OF TAPO-5 MOLECULAR SIEVE

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The conditions under which some of the Ti^{4+} ions in TAPO-5 (a titanium containing aluminophosphate) can be reduced to Ti^{3+} whilst leaving the crystal and pore structure of the molecular sieve intact, have been studied. ESR spectroscopy was used to probe the local geometry round the Ti^{3+}, and was found that this was in a distorted octahedral coordination. The heteroatom was therefore present in a separate microphase locate inside the micropores, in particles too small to be detectable by X-ray diffraction. Two titanium sites were identified. It was found that reduction of Ti^{4+} involved the lattice oxygens, whilst on exposure to air Ti^{3+} was oxidised via an electron-transfer mechanism which resulted in the formation of a superoxide.

1. Introduction

Zeolites have been the subject of extensive study in recent years in view of their great importance as industrial and laboratory scale catalysts [1,2]. Until recently, it was thought that zeolites were invariably made up of corner-sharing SiO_4 and AlO_4 tetrahedra, but it has been recognised recently that zeolitic behaviour–this is taken to mean the reversible uptake of guest molecules–is also exhibited by microporous frameworks in which the tenants of the tetrahedral sites can also be Ga, Ge, B, P, As, Ti, Zn, Fe and several other elements.

An interesting new class of microporous solids is that based on aluminium phosphate and on silico-aluminophosphate, the so-called ALPO-n [3,4] and SAPO-n [5] phases respectively. These solids have the merit of being less hydrophilic than the high-silica zeolites – but less so than the low-silica analogues, and are potentially very useful acid catalysts. Several heteroatoms have been incorporated in the ALPO-n framework, including Zn [6], Mg and Ti [7], to yield the so-called metallophosphate phases.

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As part of a continuing investigation into the properties of ALPO-n [4–6,8], we discuss here the characterisation of a Ti^{4+}-containing metallophosphate, the so-called TAPO-5 [7], which has a similar pore and crystal structure to its archetype ALPO-5. The choice was governed by the fact that Ti-silicalite, in which a small amount of Ti^{4+} has been incorporated into the silicalite lattice, is a potent catalyst for the conversion of phenol to hydroquinone and of propylene to propylene oxide [9]. TAPO-n phases have been reported to be good shape-selective catalysts for hydrocarbon conversions [7] such as cracking, alkylation, isomerisation, and reforming. Another reason for using this particular heteroatom, was that reduction of some of the Ti^{4+} ions to Ti^{3+} would enable for the first time, the study of the local environment around the heteroatom by ESR. TAPO-5 was characterised, in addition to ESR, by isothermal N_2 adsorption, thermal methods and XRD. The conditions for effective reduction of Ti^{4+} which would leave the pore and crystal structures intact, are also discussed.

2. Experimental

Preparation: TAPO-5 was prepared hydrothermally as follows: 11.2 g of pseudo-boehmite were added to a solution of 19.0 g of syrupy ortho-phosphoric acid and 17.6 g of water, and on stirring, a uniform mixture was obtained. To this, 14.8 g of titanium isopropoxide were added with thorough mixing, and finally 83.5 g of a 1% aqueous solution of the template tetra-n-propyl ammonium hydroxide. The mixture was heated at 473 K for 6 days, and the product was then filtered off, washed thoroughly and dried at 400 K.

Activation: In order to remove the organic template from TAPO-5, this was heated to 753 K under vacuum at a rate of 5 K min^{-1} followed by exposure to a flow of oxygen at that temperature, for 5 days. The resulting white powder gave a similar X-ray diffraction pattern as the as-prepared TAPO-5, whilst its N_2 adsorption isotherm showed it to be microporous. This sample gave no ESR signal near $g = 2.0$ at 293 and 77 K. Such signals have been observed in samples containing carbonaceous material, arising from incomplete template removal. The absence of template was also confirmed by thermal analysis. Calcination at 773 K in air did not remove the template cleanly, nor did treatment with methanolic HCl, a treatment which has been successful for ALPO-5 [10].

ESR measurements: ESR spectra were recorded on a Varian E3 X-band spectrometer at 293 and 77 K, and on a Varian E-109 X-band instrument at 3.6 K.

3. Results and discussion

Elemental analysis by atomic absorption spectroscopy showed that the Ti content of TAPO-5 was 5%, expressed as TiO_2. The unit cell composition was shown to be $(Ti_{0.05}Al_{0.525}P_{0.425})O_2$, which is well within that allowed by the phase diagram reported in the pertinent Union Carbide patent [7]. The absence of an ESR signal from a fresh template-free TAPO-5 confirms that titanium is in the +4 state. The N_2 adsorption isotherm of TAPO-5 is of the type I in the BDDT classification, which is characteristic of microporous solids. Some hysteresis is observed above $p/p_0 = 0.6$ which is associated with the aggregate structure of the sample, but there, unlike ALPO-5, no low-pressure hysteresis. The surface area for TAPO-5 was found to be 161 m^2g^{-1}, which is significantly lower than that for ALPO-5 (330 m^2g^{-1}) [5]. It is noteworthy that ZAPO-5, in which Zn is present in some of the Al sites in the framework, also has a lower surface area (250 m^2g^{-1}) [6] than ALPO-5. The pore volume for TAPO-5 at $p/p_0 = 0.85$ was 0.11 cm^3g^{-1}, compared with 0.21 cm^3g^{-1} for ALPO-5. This value of p/p_0 was chosen because it is the highest value for which there is no multilayer adsorption

The reduction of titanium in TAPO-5 was attempted in a temperature-programmed reduction (TPR) apparatus, in a Ar/H_2 gas stream flowing at 40 cm^3 min^{-1}. The sample was heated at rate of 5 K min^{-1} to 773 K. No change was observed in the TPR profile, which is a measure of the consumption of hydrogen,

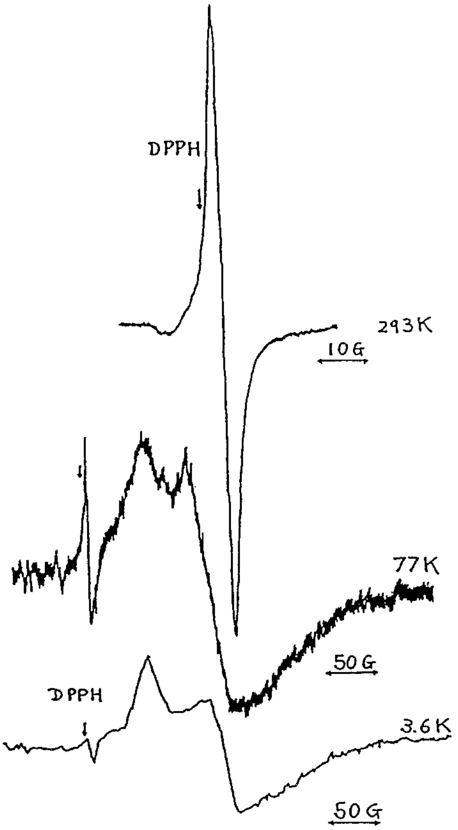

Fig. 1. ESR spectra for TAPO-5 heated in an Ar/H_2 atmosphere, recorded at 293, 77 and 3.6 K.

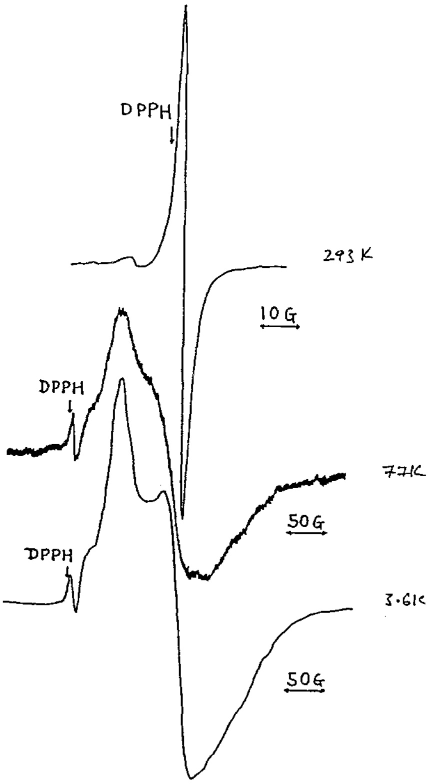

Fig. 2. ESR spectra of TAPO-5 heated in an Ar atmosphere, recorded at 293, 77 and 3.6 K.

during this treatment. The X-ray diffractogram of TAPO-5 was also unaffected by this treatment, but a strong electron spin resonance spectrum was observed. At 293 K, the spectrum consists of a single narrow line with a peak-to-peak width of ca 0.2 mT. At 77 and 3.6 K, the spectra showed an intense broad resonance at higher magnetic field, with fine structure (see fig. 1). Figure 2 shows the spectra for TAPO-5 heated in Ar in the absence of hydrogen. With respect to the narrow line at $g = 2.0025$, this can be assigned to small amounts of organic impurities which had been adsorbed by the sample on standing in the laboratory. The intense resonance at 77 K in figs. 1 and 2, however, can be attributed to Ti(III); this is confirmed by the fact that known g-values for Ti(III) never exceed that of the free electron (g_e) [11]. Given that generation of Ti(III) occurs even when TAPO-5 is heated in Ar, it is suggested that the electrons are supplied by the lattice oxygens, with the evolution of O_2. The oxygen vacancy can be refilled by further reaction of the released oxygen leaving behind a hole, which would not be detectable by ESR. This proposed reaction also accounts for the fact that in TPR, no consumption of hydrogen is observed. Additional support is given by the report of similar reduction occurring in TiO_2-SiO_2 glasses in a H_2/N_2 atmosphere of varying hydrogen partial pressure [12].

The line-shape of the resonance assigned to Ti(III) in TAPO-5 is more complex than that for Ti(III) in zeolite [13] or silica [14], where it is present as exchangeable cations. Examination of figs. 1 and 2 reveals that the Ti(III) spectrum consists of two groups of lines with $g_1 = 1.9901$, $g_2 = 1.9484$ and $g_3 = 1.8743$, and $g_1 = 1.9690$, $g_2 = 1.9254$ and $g_3 = 1.9001$ respectively. This analysis is based upon a computer simulation [15,16], in which spectral curves calculated for species with the g-values given above were superimposed with appropriate intensity ratios. It is therefore suggested, that in TAPO-5 there are two distinct sites for titanium.

From the known structure of ALPO-5 [17] it would be logical to assume that if the titanium ions are part of the aluminophosphate lattice then they should be in a tetrahedral environment, which would imply a g-value equal to g_e. In the present case, it is apparent that the g-values do not satisfy this condition. If, however, it is assumed that Ti(III) is located in distorted octahedral sites, the g-values obtained are reasonable. The g-values can be expressed as

$$g_x = g_e - 2\lambda/\delta_1 \qquad (1)$$

$$g_y = g_e - 2\lambda/\delta_2 \qquad (2)$$

and

$$g_z = g_e - 8\lambda/\Delta_{\text{oct}} \qquad (3)$$

in the case a distorted octahedral field with D_{2h} symmetry [18], where λ is the spin-orbital coupling constant, Δ_{oct} the major octahedral crystal field splitting, and δ_1 and δ_2 the subsidiary splitting due to minor distortions. The observed deviations of the g-values from g_e for the two sets of signals are in fair agreement with expressions (1) to (3). Therefore, it appears that in TAPO-5 the titanium atoms are in a distorted octahedral configuration, in which two ligand *trans* to each other are similar, and different from the two other non-equivalent pairs. Titanium in a distorted octahedral field of D_{2h} symmetry is somewhat uncommon, and thus the ESR spectra obtained here are dissimilar to those obtained for titanium-exchanged zeolites [19].

The most likely explanation for these observations is that titanium is present as a guest species inside the channels of the ALPO-5 framework. This is corroborated by the lower surface area of TAPO-5 compared to ALPO-5, although similar reductions in surface area compared with the equivalent ALPO-n phase have been observed for other metallophosphates. Attempts to ion-exchange the titanium out of the structure failed, which means that the titanium ions are not present as exchangeable cations.

The model that is proposed, therefore, is that titanium is present as a TiO_2-like microphase which is thinly distributed inside the aluminophosphate pore structure. The similarity of the TAPO-5 X-ray diffractogram with that for ALPO-5 precludes the existence of a separate TiO_2 phase. The lower apparent surface area for TAPO-5 as compared with ALPO-5 is consistent with this narrowing of the pores. The islets (particles) of TiO_2 structure mentioned above, would be too small to be observed by X-ray diffraction. Further, the fact that there is no significant change in the diffractogram of TAPO-5 before and after calcination, probably indicates that there is very little migration of heteroatoms out of the tetrahedral lattice on heating. The lack of isomorphous substitution would also explain the absence of cation exchange capacity, which would be expected for a non-stoichiometric solid such as TAPO-5.

The fact that two ESR signals have been observed, can be interpreted as being due to Ti surrounded by four ---O---Ti groups, and either two ---O---Al, or two ---O---P ones. It is thus suggested that the TiO_2 microphase is anchored to the host lattice by Ti---O---Al and Ti---O---P bonds. These bonds would be polarised, and would provide sites capable of specific adsorption. Evidence of this is seen in the adsorption isotherm, which shows high rectangularity at low p/p_0 (ie a high degree of adsorption close to $p/p_0 = 0$), which is characteristic of the existence of specific adsorption sites. Such sites are not present in ALPO-5, and if Ti were present as exchangeable cations it would not be expected to give rise to such.

The Ti(III) ESR spectra reported so far have been recorded without the samples being allowed to come in contact with the atmosphere. The ESR

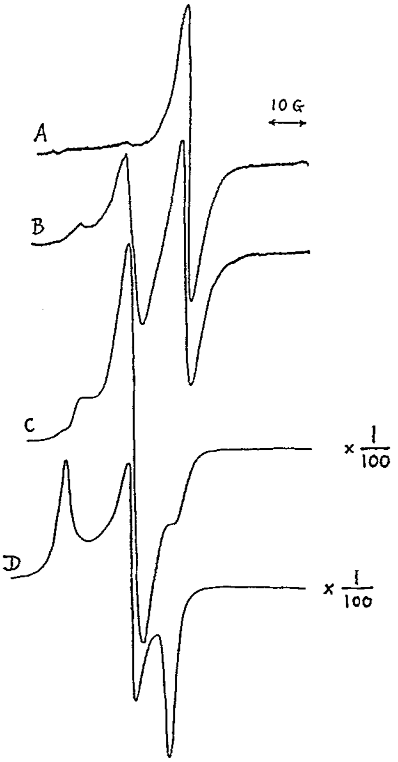

Fig. 3. ESR spectra of reduced TAPO-5 (a) freshly prepared, (b) after 30 minutes, (c) 12 hours, and (d) exposure to air for 6 hours.

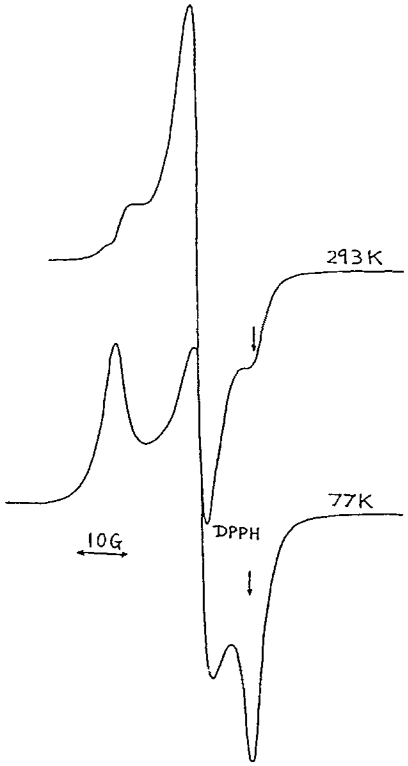

Fig. 4. ESR spectra of reduced TAPO-5 at 293 and 77 K.

spectrum of reduced TAPO-5 was recorded at 293 K, after exposure to the atmosphere. A new signal was obtained at $g = 2.0110$ in addition to that due to the organic impurities, which remained unchanged. On longer exposure to air, an intense signal with shoulders developed at $g = 2.0104$ (see fig. 3). On lowering the temperature to 77 K, a signal which has been assigned to the superoxide of titanium (IV) appeared ($g = 2.0194$, 2.0094, 2.0034), with the simultaneous disappearance of the titanium (III) signal. It appears that a superoxide is formed via electron transfer between Ti(III) and a neighbouring oxygen atom, which could be part of the lattice (see fig. 4). The spectra are reversible with temperature change. A similar signal with three different g-values is observed at ambient temperature by further exposure of TAPO-5 in air, confirming the presence of a superoxide. Presumably, the two resonances which appear close to one another at $g = 2.0213$ and 2.0194 upon prolonged exposure to the atmosphere are due to the superoxides of titanium in the two different environments discussed above; it has been shown by others that this resonance is very sensitive to the environment of the superoxide [20].

The fact that the oxygen of the lattice is mobile enough to allow reaction to take place – it is unlikely that water is present in the pores in large quantities under the experimental conditions used – and that electron mobility exists between the metal cation and the oxide framework augurs well for the usefulness of metallophosphates as catalysts.

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