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^{57}Fe Mössbauer Spectroscopic Studies of the Ferrocene Molecular Reorientation in $AlPO_4$-5 and $AlPO_4$-8 Frameworks

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^{57}Fe Mössbauer spectroscopic studies were carried out on ferrocene guest molecules in some microporous aluminium phosphate host lattices in order to investigate their behaviour in the aluminium phosphate channels. The 300 K spectra show broad single lines with isomer shifts of 0.39 and 0.41 mm s^{-1} relative to iron for $AlPO_4$-5:ferrocene and $AlPO_4$-8:ferrocene inclusion compounds, respectively.

The absence of quadrupole splittings for these materials contrasts with the large quadrupole splitting observed for ferrocene itself at the same temperature. The low-temperature spectrum (20 K) for $AlPO_4$-5:ferrocene shows a doublet with quadrupole splitting of 2.37 mm s^{-1} and an isomer shift of 0.55 mm s^{-1}. The collapse of the quadrupole splitting at room temperature is consistent with the ferrocene molecules rotating within the channels.

Zeotypic materials such as zeolites and the microporous aluminium phosphates are currently of much interest because of their catalytic and molecular sieving properties.[1–3] These properties arise in part from the presence of well defined channels and pores within the solid host structures. There is also the possibility of using such structures to incorporate different guest molecules, for example as precursors for metal-based catalysts. We are interested in the behaviour of guest molecules included in zeotypes. Specifically, one of these systems involves ferrocene as the guest molecule and a large-pore structure aluminium phosphate (AlPO) as the host. The thermal and hydrothermal stabilities of $AlPO_4$-5 and $AlPO_4$-8 are excellent (e.g. the materials withstand calcination at 1000°C),[4] which makes these materials promising candidates for some industrial applications. Another large-pore AlPO that is known is designated VPI-5.[5] The VPI-5 structure transforms to $AlPO_4$-8 at temperatures $\geq$60°C.[6]

To date, ferrocene has been included in other channel hosts such as thiourea[7–9] and zeolite Y,[10] and these materials have been investigated by ^{57}Fe Mössbauer and ^{2}H NMR spectroscopy, and by extended X-ray absorption fine structure spectroscopy (EXAFS), respectively. No corresponding studies on zeotypic AlPOs have been reported. We have therefore undertaken a ^{57}Fe Mössbauer study on the ferrocene inclusion compounds with $AlPO_4$-5 and $AlPO_4$-8.

^{57}Fe Mössbauer spectroscopy is a useful tool for probing the electronic environment of iron-containing guests in zeotypic materials. Taken together, Mössbauer spectroscopy and structural information from other methods, such as X-ray crystallography and EXAFS, are a powerful combination, because the former provides information on electron distributions at a probe nucleus which is particularly enhanced when viewed in the light of accurate structural details provided by the latter.

Experimental

$AlPO_4$-5 and VPI-5 were prepared by hydrothermal syntheses analogous to the literature procedures.[11–13] $AlPO_4$-8 was obtained by calcining VPI-5 at 600°C. All the $AlPO_4$ molecular sieves were activated before use by calcining first at 600°C for 24 h, and then heating them to 300°C for 6 h whilst they were being evacuated. Ferrocene was incorporated into the $AlPO_4$ frameworks by impregnating the host solids with saturated solutions of ferrocene in pentane.

Atomic absorption spectroscopy (AAS) carried out on a Perkin-Elmer Zeeman 5100 instrument shows that

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absorption of ferrocene into the channels of both AlPOs is under 0.7% for Fe.

The structures of the products and their precursors were confirmed by X-ray powder diffraction (XRD) using a Philips X-ray generator, Cu$K\alpha$ radiation and a graphite crystal monochromator.

The Mössbauer spectra were recorded using a spectrometer of the Harwell 6000 series with a Harwell proportional counter and a ^{57}Co in Rh source. Spectra were calibrated against iron foil at room temperature, and computer fitted to Lorentzian peaks.

Results and discussion

The channel inclusion compounds. The colours of the $AlPO_4$-5:ferrocene and $AlPO_4$-8:ferrocene inclusion compounds are different. The former is green whilst the latter has the yellow–brown colour of ferrocene itself. We note that the corresponding silicon-substituted aluminium phosphate, $SAPO_4$-5:ferrocene[14] is also yellow–brown. Clearly, the difference in colour has to be explained.

It is known that under acidic conditions ferrocene oxidises to the ferricenium cation, $Fe(Cp)_2^+$ the colour of which is blue for dilute samples, whilst concentrated samples are red.[15]

Since the only difference between $AlPO_4$-5 and $AlPO_4$-8 is structural, the reason for the difference in colour must be associated with the manner in which ferrocene interacts with the frameworks. This difference can be narrowed down to electronic effects because $SAPO_4$-5 is isostructural with $AlPO_4$-5. The aluminium phosphate frameworks are built up of alternating $Al(O)_4$ and $P(O)_4$ tetrahedra whose formal charges are mutually compensated.

Thus, these materials have neutral frameworks without any ion-exchange properties or strong acid sites (with the possible exception of some metal-substituted AlPO compounds).[16,17] In the specific case of $AlPO_4$-5 there appears to be some weak acidity, which has been attributed to lattice imperfections.[18–20] This property is relevant to the present study.

Our explanation for the green $AlPO_4$-5:ferrocene colour is that a small proportion of the included ferrocene molecules have been oxidised to ferricenium cations at a few local acidic sites within the channels, thereby causing the change in colour from yellow–brown to green. That the proportion of ferricenium is small is consistent with the fact that this ion is observed in the low-temperature Mössbauer spectra but not in the EXAFS (see below).

Substituting Si(IV) into the framework poses the problem of ascertaining the location of this atom, i.e. does it substitute for Al(III), P(V) or both? If Si(IV) for Al(III) the charge in the framework charge will be positive and anion-exchange properties will be present. Substituting P(V) leads to negative framework sites and hence acidity. No overall change in framework will occur if both Al(III) and P(V) are substituted. The acidic behaviour of a number of SAPOs is consistent with P(V) substitution. $SAPO_4$-34 and $SAPO_4$-37 have mole fractions for $Si_xAl_yP_z$ $(x+z=y)$ that indicate substitution for phosphorus. For $SAPO_4$-5 there is evidence for substitution of two silicon atoms for aluminium and phosphorus (and $x+z>y$), giving overall neutrality.[21] Whatever the explanation, there is a clear difference between the isostructural $AlPO_4$-5 and $SAPO_4$-5 with regard to their interactions with a small proportion of the ferrocene molecules.

The frameworks. X-Ray powder diffraction confirms that the products are hexagonal $AlPO_4$-5 and orthorhombic $AlPO_4$-8 with cell parameters: $a=b=13.697(1)$, $c=8.375(1)$ Å and $\gamma=120°C$ and $a=33.29(2)$, $b=14.76(2)$ and $c=8.257(4)$ Å, respectively. The $AlPO_4$-5:ferrocene and $AlPO_4$-8:ferrocene give XRD patterns which closely match those for the AlPOs themselves. The cell parameters for $AlPO_4$-5:ferrocene; $a=b=13.753(2)$, $c=8.410(3)$ Å and $\gamma=120°C$ are consistent with the $AlPO_4$-5 framework being essentially unmodified by the guest molecules. The small changes in cell parameters reflect only minor changes as the framework adjusts to the guest molecules. The cell parameters for $AlPO_4$-8:ferrocene are: $a=32.269$, $b=14.824$ and $c=8.320$ Å, the orthorhombic cell of $AlPO_4$-8:ferrocene is expanded in the b- and c-directions, whereas the a-direction is contracted.

Mössbauer parameters. The Mössbauer parameters of interest in this connection are the isomer shift (δ) and the quadrupole splitting (ΔE_Q). The isomer shift is a measure of the total s-electron density at the probe nucleus. Factors influencing isomer shifts[22] include the delocalisation of 4s-electron density into bonding levels, the radial expansion of the 4s orbital, which is an expression of covalency in the bonding, and the use of 3d and 4p orbitals which, because of their shielding properties, modify the total s-electron density at the probe nucleus. As expected for dilute systems, the Mössbauer effect signal is weak (2% relative absorption), but the spectra are adequate to establish that the isomer shifts, δ for $AlPO_4$-5:ferrocene and $AlPO_4$-8:ferrocene at room temperature, are close to that for ferrocene itself (0.39 and 0.41 mm s^{-1} for $AlPO_4$-5 and $AlPO_4$-8, respectively). In both cases, slightly broadened single lines ($\Gamma=0.42$ and 0.52 mm s^{-1}) were seen (Fig. 1). The feature of interest for the room-temperature spectra for both materials is the absence of a quadrupole splitting. The Mössbauer parameters are given in Table 1. However, at low temperature (20 K) $AlPO_4$-5:ferrocene does show a spectrum (ΔE_Q of 2.37 and δ of 0.55 mm s^{-1}) that is characteristic of ferrocene itself. There may be evidence for a significant presence of ferricenium (25%).

Clearly, the only difference between the room-temperature and 20 K spectra is the temperature-dependent quadrupole splitting. In general, the quadrupole splitting contains information on the relative distribution of Fe 3d and

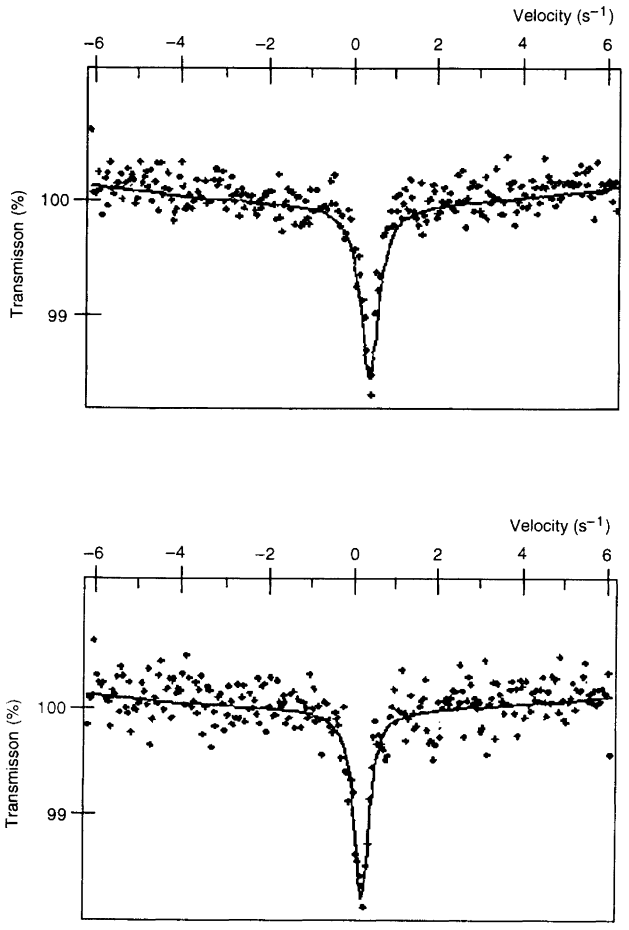

Fig. 1. Room temperature ^{57}Mössbauer spectra for $AlPO_4$-5:ferrocene (above) and $AlPO_4$-8:ferrocene (below).

4p electron densities over all the bonds. In covalent compounds such as ferrocene, the major contribution to quadrupole interactions at the iron nuclei arises out of subtle imbalances in the 3d and 4p orbital occupations (i.e. each orbital set is non-degenerate because of deviations of the electronic environments from cubic symmetry). For cubic electronic symmetries (and of course spherical symmetry for a hypothetical isolated atom or ion) there is no electric field gradient because the 4p orbital is degenerate and the 3d orbitals split into two degenerate sets.

However, it is a caveat that, whereas a cubic environment cannot possess an electric-field gradient, the reverse is not necessarily true. Cases are known[22,23] in which non-cubic crystallographic sites produce what might be termed *pseudo* cubic electronic environments in which the p/d orbital degeneracy is hardly lifted within spectral resolution, i.e. there is no significant imbalance.

This is not the case for $AlPO_4$-5:ferrocene and $AlPO_4$-8:ferrocene inclusion compounds, because the iron nuclei are in non-cubic environments (specifically, the immediate environment is either D_{5h} or D_{5d}). This is demonstrated by the fact that a large quadrupole splitting is observed at low temperature, the magnitude being the same as for ferrocene itself. Hence, the Mössbauer parameters for the inclusion compounds are indistinguishable from those for ferrocene. The singlet observed at room temperature does not actually indicate a cubic environment, but is consistent with another effect: dynamic orientation. This effect can be explained on the basis of the dynamic behaviour of ferrocene in the host channels, an explanation which is the same as that given for the thiourea:ferrocene inclusion compound.[7,8,14] The rapid orientational changes average the electric field gradient to zero, during the time of observation, 10^{-8} s^{-1} for ^{57}Fe.

Table 1. ^{57}Fe Mössbauer effect spectral parameters[a] of iron in AlPO-5:ferrocene and AlPO-8:ferrocene channel inclusion compounds and literature values for ferrocene and iron complexes.

Compound	Authors and reference	ΔE_Q[b]/ mm s^{-1}	δ[c]/ mm s^{-1}
AlPO-5:Fe(CP)$_2$	This paper (300 K)	0	0.39
AlPO-5:Fe(CP)$_2$	This paper (20 K)	2.37	0.55
AlPO-8:Fe(CP)$_2$	This paper (300 K)	0	0.41
Fe(CP)$_2$	Zahn *et al.*[28] (RT)[d]	2.34	0.52
Fe(CP)$_2$	Wertheim[29] (298 K)	2.36	0.60
Fe(CP)$_2$	Epstein[30] (78 K)	2.40	0.46
[Fe(CP)$_2$dtc]$_3$	Fiddy *et al.*[31] (295 K)	0.25	0.39
Thiourea:Fe(CP)$_2$	Lowerey *et al.*[7] (RT)[d]	0	0.50
Thiourea:Fe(CP)$_2$	Lowerey *et al.*[7] Low temperature (110 K)	2.40	0.52
Ferricenium salts:			
Tetrafluoroborate	Zahn *et al.*[28] (RT)[d]	0.76	0.54
Picrate	Epstein[30] (78 K)	0.00	0.53

[a]Isomer shift relative to room temperature natural iron foil. [b]ΔE_Q=quadrupole splitting. [c]δ=isomer shift. [d]RT=room temperature.

Previous studies have been carried out on ferrocene (guest) in thiourea (host) systems,[7-9] $CdPS_3$[24] and in cyclodextrin.[25] The most thoroughly studied case is the thiourea:ferrocene clathrate, in which ferrocene appears to have complete three-dimensional rotation at 1000 K, and even at room temperature. The molecular reorientational dynamics of ferrocene included in the thiourea lattice have been studied by ^{2}H NMR and Mössbauer spectroscopy[7,8] and ^{13}C CP/MAS NMR,[9] and by molecular mechanics, molecular dynamics and Monte Carlo simulations.[14] In all these studies the guest molecule adopts parallel and perpendicular orientations in the host channel. The channels in the thiourea host lattice are 10 Å in diameter,[26] allowing considerable room for rotating ferrocene guest molecules (effective diameter ca. 7 Å).

In the two present materials, the channel diameters are 7.9 Å and 7.9 × 8.7 Å for $AlPO_4$-5[16] and $AlPO_4$-8,[27] respectively. This considerably reduces room for movement. Nevertheless, the room-temperature spectra do show complete orientational (including flipping between parallel and perpendicular orientations) freedom which is still rapid on the Mössbauer timescale (Fig. 1),

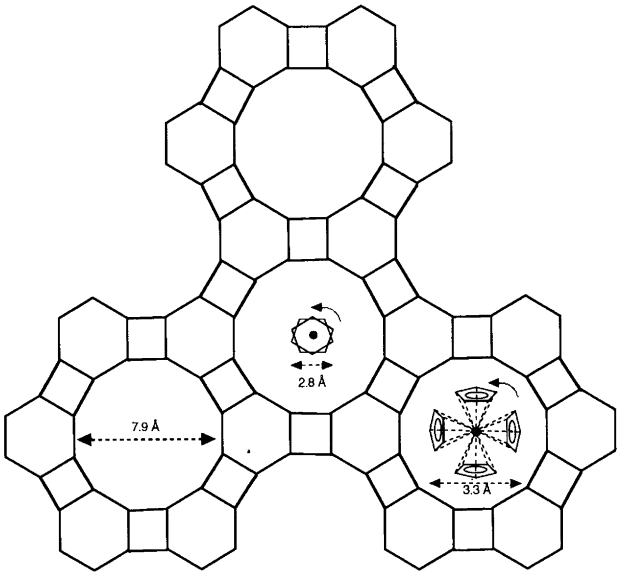

Fig. 2. A simple representation of an $AlPO_4$-5 channel (diameter 7.9 Å) (left), and its size in relation to the parallel orientated ferrocene guest molecule (middle) and the perpendicular orientated ferrocene (right). The curved arrows indicate the motion of the guest molecule.

whereas the low-temperature spectrum shows either fixed molecules or rotations that are slow on the Mössbauer timescale. Figure 2 shows the orientations of ferrocene guest molecules in the $AlPO_4$ host channels.

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