The architecture of Mg(II) centres in MAPO-36 solid acid catalysts

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The local structure around Mg^{2+} ions of a Magnesium substituted aluminophosphate, with the ATS structure (MgAPO-36, Mg/P=0.08), in the as-prepared and calcined state has been investigated by Mg K-edge XAS spectroscopy. High quality XAS data were collected using the solid-state fluorescence detector. Mg^{2+} is found to replace tetrahedrally co-ordinated Al^{3+} in the as-prepared state and remained intact even after calcination, thus yielding a highly active, solid acid catalyst.

Keywords: Magnesium Aluminophosphate, Acid catalysis, XAS

1. Introduction.

The substitution of small amounts of divalent metal ions in place of Al^{3+} in microporous aluminophosphates can be utilised to introduce redox and/or acidic centres, which are uniformly distributed throughout the framework producing powerful and shape selective heterogeneous catalysts. The catalytic properties depend crucially on the nature of substitution. When these ions are present in the framework sites, upon removal of the charge compensating organic template molecules, a loosely bound proton is attached to the bridging oxygen, to charge balance the overall negative charge due to the presence of divalent ions. Thus, it is important to determine the nature of substitution of the divalent ions to evaluate the ability of these materials for catalytic applications. X-ray diffraction, although essential in determining the overall structure to understand the shape selective properties of these solids, is not completely useful, since the amount of divalent ions incorporated is usually low (less that 10 percent) and they are distributed randomly in the structure without possessing any long-range order. X-ray absorption spectroscopy, on the other hand, provides the required structural information, since this technique does not depend on the long-range order. This technique has been successfully used in various transition metal substituted materials [Sankar and Thomas, 1999, Sankar, Thomas and Catlow, 2000]. However, recording high-quality EXAFS data for magnesium containing solids have been a problem due to the low concentration of the metal ions and the data collected by electron yield method was not satisfactory; in some cases it was restricted only to the XANES part of the XAS data [See for example, Howe *et al*, 2000, Presented in this conference]. It is therefore, our aim to use Mg K-edge X-ray absorption spectroscopy to determine the charge state as well as the local coordination environment of magnesium ions in the Mg^{2+} substituted aluminophosphate, MgAlPO-36 material. With the recent developments at Daresbury Laboratories in both the

measurement of Mg K-edge EXAFS data by the fluorescence method as well as the introduction of a recently developed heating system, it was possible to obtain high-quality Mg K-edge XAS data to determine the local structure of the Mg^{2+} ions[Smith et al 1998]. This study clearly shows that Mg^{2+} ions are present in tetrahedral environment in both the as-prepared and calcined state.

2. Experimental

2.1 Synthesis.

Monophasic MgAPO-36 was prepared using the procedure described in Wright et al (1992). $MgAl_2O_4$ was prepared using the standard nitrate decomposition route, and MgO was obtained from Aldrich.

2.2 Characterisation.

Mg K-edge EXAFS measurements were carried out at Station 3.4 of the Daresbury Laboratory, which operates at 2 GeV with a typical current of 150-250mA. Station 3.4, was equipped with a double crystal beryl monochromator. Multiple scans collecting both the total electron and fluorescence yields (using a single element solid state detector) were obtained for each of the materials. The samples were mixed with graphite, pressed to form a self supporting wafer and then mounted onto the sample holder using double-sided graphite tape. We used a Beryl double crystal monochromator in these experiments, as although $YB_{66}(400)$ crystals are often preferred for XAS measurements below 2 keV, the presence of two pronounced features in the Mg EXAFS spectra at 1385 and 1437 eV, attributed to a spurious reflections from the (600) plane (Tanaka *et al*, 1997) makes the collection of good quality EXAFS data extremely difficult (Smith *et al*, 1998). Furthermore, due to the low concentration of Mg in the MAPO-36 material, the use of the total electron yield method for collection of EXAFS gives spectra with a very poor signal to noise ratio. Thus, we used the fluorescence data, which gave far superior XAS data quality.

Calibration, and background subtraction of the data was undertaken using the programs EXCALIB and EXBROOK, available at the Daresbury Laboratories, U.K. Final data fitting was carried out using the EXCURV98 program. (Binsted *et al*, 2000). Phase-shift calculations were carried out using the ground state potential and phase shifts (Barth and Hedin, 1972; Hedin and Lundquist, 1969). EXAFS analysis was undertaken for the first shell only using the single scattering curved wave approximation, since the data range was limited due to the presence of large amounts of aluminium in the sample.

XRD patterns were collected using a Siemens D5000 diffractometer using Cu Kα radiation. FTIR spectra were recorded on a Perkin-Elmer 1725X spectrometer using an in-situ cell (Barrett *et al*, 1996). Elemental analyses were obtained by ICP analysis (Kingston Analytical Services).

3. Results and Discussion

The X-ray diffraction patterns of the materials studied confirmed the presence of monophasic and highly crystalline MgAPO-36. Furthermore, no collapse of the microporous framework of the MgAPO-36 sample was observed upon calcination (to remove the organic template molecule). Chemical analyses confirmed a

Mg/Al ratio of 1:2 for the magnesium aluminate standard, and a Mg:P ratio of 0.08 : 1 ratio for the MgAPO-36 material.
First we discuss the EXAFS results of the standard materials and subsequently the MgAlPO-36 catalysts.

3.1 XAS Studies of MgAl$_2$O$_4$ and MgO standards..

MgO and MgAl$_2$O$_4$ were utilised as model compounds to determine the structural parameters for Mg^{2+} in an octahedral and tetrahedral environment, respectively. Spinel structures are often used as model compounds for metal substituted alumino-phosphates [Barrett et al, 1996]. However, MgAl$_2$O$_4$, as opposed to MgCr$_2$O$_4$, was specifically chosen in this instance, because not only it has been shown that this material contains Mg^{2+}, entirely, in tetrahedral co-ordination (Sasaki *et al*, 1979), but also, like the MgAPO-36 materials it also contains aluminium. This is very important because the Al-K edge is only some 250 eV above the Mg-K edge and thus substantially reduces the data range of the Mg EXAFS leading to significant truncation effects and errors in the derived EXAFS parameters.   A total of four scans were collected and averaged for each sample. The derived structural parameters for these materials are given in Table 1. The corresponding EXAFS plots and their Fourier transforms are given in Figures 1 and 2 for MgO and MgAl$_2$O$_4$, respectively. The derived Mg-O distances (see Table 1) show good agreement with those obtained from the crystal structures of these materials (2.109 Å and 1.922 Å for MgO and MgAl$_2$O$_4$ respectively)
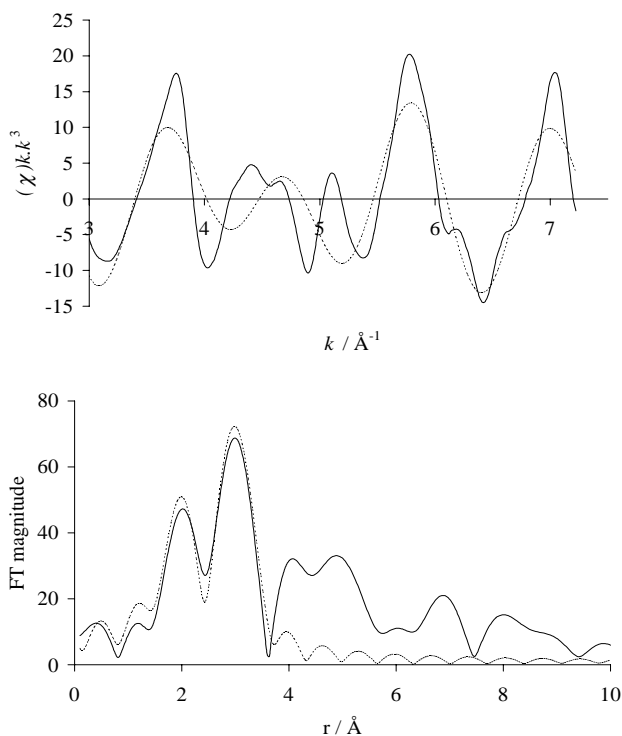

Figure 1
Mg-K edge EXAFS fit (top) and associated Fourier transform (bottom) for MgO standard. [Experimental data (—), theory (- -)].

Standard	Oxygen environment	$R(Mg\text{-}O)$ / Å	$2\sigma^2$ / Å^{-1}
MgAl$_2$O$_4$	Tetrahedral	1.958	0.010
MgO	Octahedral	2.128	0.024

Table 1
Structural parameters of tetrahedral (MgAl$_2$O$_4$) and octahedral (MgO) standards obtained from Mg-K edge EXAFS data. $R(Mg\text{-}O)$ is the Mg-O inter-atomic distance, and $2\sigma^2$ the Debye - Waller factor.
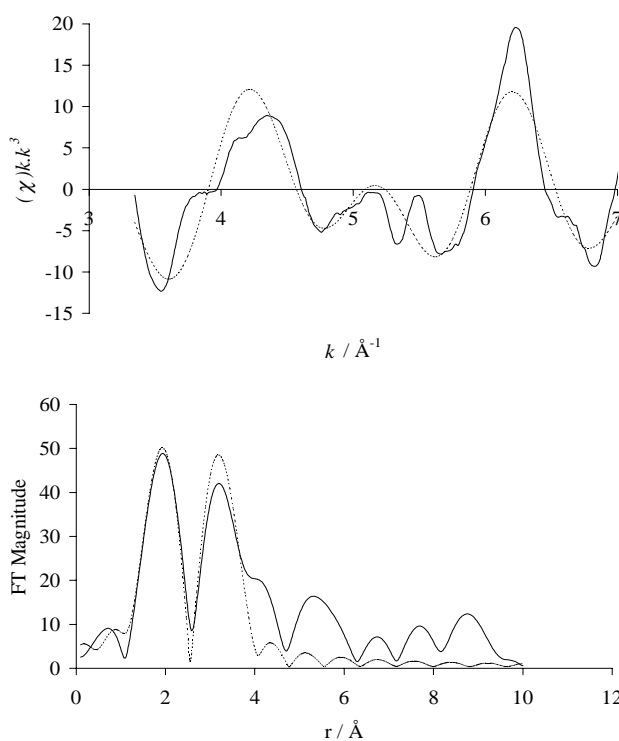

Figure 2
Mg-K edge EXAFS fit (top) and associated Fourier transform (bottom) MgAl$_2$O$_4$ standard. [Experimental data (—), theory (- -)]

3.2 XAS Studies of MAPO-36 catalysts.

Mg K-edge EXAFS data were analysed using a procedure similar to that used for the standards using an identical k-range, and without Fourier filtering the data.
 It must be noted, however, that these materials readily adsorb water that can only be desorbed at high temperatures. Thus, unless the catalyst is dehydrated *in-situ,* prior to recording the XAS measurement (as was done in this case), a third possible Mg environment (apart from the regular tetrahedral and octahedral coordination geometries) consisting of four oxygen's with bond distances typical of those seen for the tetrahedral site, and two extra oxygen at ca 2.4 Å attributable to the loosely bound water molecules, should be considered as a possible model for the analysis of the EXAFS data.
Refinement of the values of the inter-atomic (Mg-O) distances, the Debye-Waller factors and Eo were carried out starting from each of the possible three models to yield the best fit. The derived structural parameters for the best fit for our MgAPO-36 catalyst (Mg/Al 0.08) before and after calcination are given in Table 2. The corresponding EXAFS plots and their Fourier transforms are
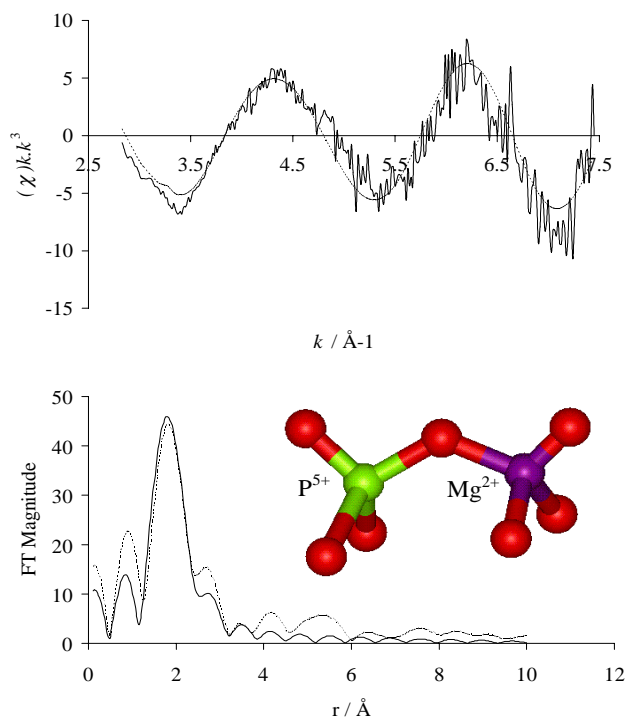
Figure 3
Mg-K edge EXAFS fit (top) and associated Fourier transform (bottom) for MAPO-36 catalyst before calcination. [Experimental data (—), theory (- -)], (inset) Schematic model of Mg^{2+} site present in as-synthesised catalyst

calcination (to remove the occluded template and activate the catalyst) yielding a material which is a good solid-acid catalyst.
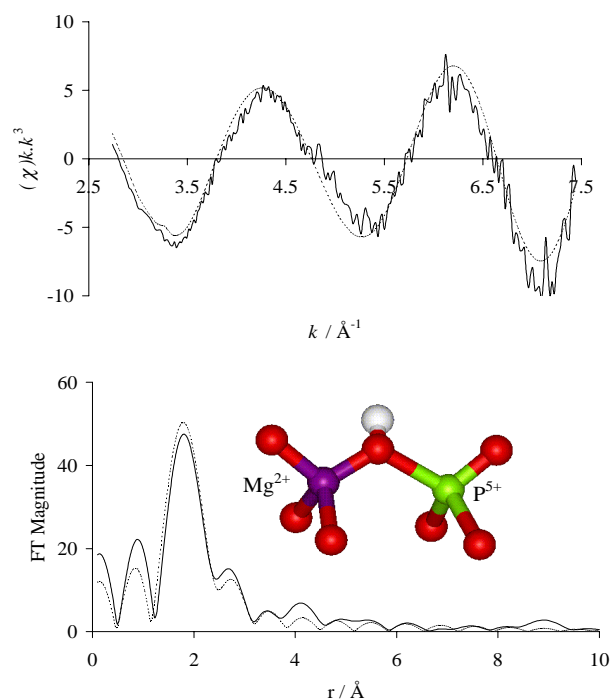

Figure 4
Mg-K edge EXAFS fit (top) and associated Fourier transform (bottom) for MAPO-36 catalyst after calcination. [Experimental data (—), theory (- -)], (inset) Schematic model of Mg^{2+} site present in calcined catalyst.

given in Figures 3 and 4 for MgAPO-36 before and after calcination, respectively. The derived structural parameters for the MgAPO-36 catalyst before calcination, indicates that there are four oxygen's at 1.935 Å in the first coordination sphere around the magnesium. Comparison of the Mg-O distances with those obtained for the standard materials indicate that magnesium is present in the framework, in place of a tetrahedrally co-ordinated Al^{3+} ion. After calcination of the MAPO-36 catalyst, it can be seen that the Mg-O distances are almost identical to those in the as prepared material. Therefore, the magnesium ions are likely to be present in the framework after calcination. Thus as the x-ray diffraction pattern indicates that the long range structure is preserved on calcination, and EXAFS indicates that the Mg^{2+} is retained in a tetrahedral framework position it is expected that this material will be a good catalyst. Furthermore, although it was shown in the case of cobalt substituted CoAlPO's [Barrett et al 1996] that upon introduction of acidic proton, the tetrahedral site is in a distorted environment, a similar detailed study is not possible in the case of magnesium, since the available data range is rather restricted due to the presence of aluminium, as mentioned earlier. EXAFS analysis starting from the hydrated model, gave non sensible values for the Debye-Waller factor of the oxygen's attributed to water and a poorer fit to the experimental data than that obtained for the dehydrated model.

We have shown that high quality Mg-K edge EXAFS data can be obtained from a material containing low concentrations of Mg using the solid state soft-energy fluorescence detector on station 3.4 of the Daresbury Laboratories, U.K. The use of MgO and $MgAl_2O_4$ standards has allowed us to determine that Mg^{2+} substitutes directly into the aluminophosphate lattice in place of tetrahedral Al^{3+} in MAPO36. This geometry is retained upon

Material	N and type	R / Å	$2\sigma^2$ / Å^{-1}
MAPO-36 (As prepared)	4 x O	1.935	0.012
MAPO-36 (Calcined)	4 x O	1.943	0.008

Table 2
Structural parameters of MAPO-36 catalysts before and after calcination obtained from Mg-K edge EXAFS data. N is the coordination number, R is the inter-atomic distance, and $2\sigma^2$ the Debye - Waller factor. Typical errors: $N \pm 10\%$; $2\sigma^2 \pm 10\%$; $R \pm 0.02$ Å

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