

Effect of Si(IV) substitution on the stability of microporous ZnAPSO-44 solid acid catalysts: a combined XAS/XRD study

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The combined XAS/XRD technique has been used to investigate the stability of the microporous structure during calcination process for a series of ZnAPSO-44 materials. Incorporation of large amounts of Zn is found to produce materials that are unstable upon removal of the structure directing organic template molecule. However, simultaneous incorporation of Si is found to increase the thermal stability of the materials, yielding catalysts that are well suited for acid catalysed reactions.

Keywords: microporous materials, zinc aluminophosphate, XAS/XRD, catalysis, QuEXAFS.

1. Introduction

The incorporation of high concentrations of lower valent ions into tetrahedral framework sites of microporous aluminophosphates is necessary to increase the number of acid (e.g. Zn, Mg) and/or redox (e.g. Co, Fe, Mn) centres in an otherwise neutral framework. The materials with the highest acidity are those that contain the largest concentration of metal ions, though, as has been shown previously in the case of cobalt this often makes them unstable (loss of open framework structure) during thermal activation yielding dense phase materials with no catalytic activity (Barrett *et al.*, 1996). However, simultaneous incorporation of Si (in place of P) into the lattice is known to increase the stability of these materials (Barrett *et al.*, 1995). In addition, a change in the oxidation state of the 2+ ions to 3+ is also observed when the microporous material was made stable. Our aim is to investigate whether similar effects, in particular the structural stability, can be introduced in the case of Zn substituted aluminophosphates. For this purpose, we have used the combined Quick XAS/XRD technique to study the effect of Si incorporation on both the long range (XRD) and local structure around Zn(XAS), *in situ*, for a series of ZnAPSO-44 materials (which have the Chabazite structure) as a function of temperature during thermal activation. In order to effectively model the changes in the static and thermal disorder of for the Zn-O atom pairs we have also collected data for ZnAl₂O₄ and ZnO standards which contain Zn²⁺ in a tetrahedral geometry. Combining the results obtained from the XRD, Zn-K edge XAS and FTIR data it was possible to understand the nature of the active site formed and the role of Si on the stability on the microporous structure.

2. Experimental

2.1 Synthesis.

ZnAPSO-44 materials were crystallised from a gel containing zinc acetate, aluminium hydroxide, phosphoric acid, and cyclohexylamine of composition xZn: (0.4-x)Si: (1-x)Al: (0.6+x)P: 1 C₆H₁₃N: 30 H₂O, where x = 0-0.4, under autogeneous pressure for up to 4 weeks at 190 °C. ZnAl₂O₄ was prepared by addition of NH₄HCO₃ to a 1:1 mixture of zinc and aluminium nitrates in solution to achieve a pH of 7.5. After filtration and washing in water, the solid was calcined in flowing O₂ at 1000 °C for 50 h. ZnO was obtained from Aldrich.

2.2 Characterisation.

QuEXAFS/XRD measurements were recorded sequentially on station 9.3 of the Daresbury Laboratory, (which operates at 2 GeV with a typical current of 150-250 mA), collecting first the XAS data for 387 sec and then the XRD data for 180 sec. with a total cycle time of 10 minutes including 33 s dead time. Station 9.3 was equipped with a vertically focussing mirror, a double crystal Si(111) monochromator, and ion chambers for measuring the incident and transmitted beam intensities. The XRD pattern was measured using an INEL position sensitive detector at an energy below the Zn-K edge to minimise background due to fluorescence. The sample (typically 50 mg) was mounted in a specially designed furnace (Catlow *et al.*, 1995) as a self supporting wafer. The sample was heated at 5 °C min⁻¹ under flowing oxygen to 350 °C, and then at 2 °C min⁻¹ to 530 °C. After holding at this temperature for up to 1 h, the sample was cooled to ambient temperature and the XRD and XAS patterns recorded once more. Calibration, background subtraction of the EXAFS data was carried out using the EXCALIB and EXBROOK programs available at Daresbury Laboratories, U.K. Curve fitting analysis was carried out using latest version of the EXCURVE program (Binsted *et al.*, 2000). *Ab-initio* calculations were used to determine 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. Calibration of the INEL position sensitive detector (PSD) was carried out using a Si standard. The lattice parameters of the materials were determined using the CELREF program (Laugier and Bochu, 2000) Laboratory X-ray diffraction measurements were performed using a Siemens D500 diffractometer using Cu K α radiation. FTIR spectra were recorded on a Perkin-Elmer 1725X spectrometer using an in-situ cell (Barrett *et al.*, 1996). Elemental analyses were obtained using ICP analysis (Kingston Analytical Services, U.K.).

3. Results and Discussion

First we discuss the results of the ZnAPSO-44 catalysts and subsequently use the results of the model compounds to explain the changes in the structural parameters derived from EXAFS. Stacked plots of the X-ray diffraction patterns recorded during the activation process for both ZnAPO-44 and (0.1)ZnAPS(0.3)O-44 are shown in Figure 1. It is clear from the XRD patterns that the reflections present in the starting material, corresponding to the Chabazitic phase is completely lost for the ZnAPO-44 sample, above *ca* 400 °C. Whereas for the ZnAPSO-44 the

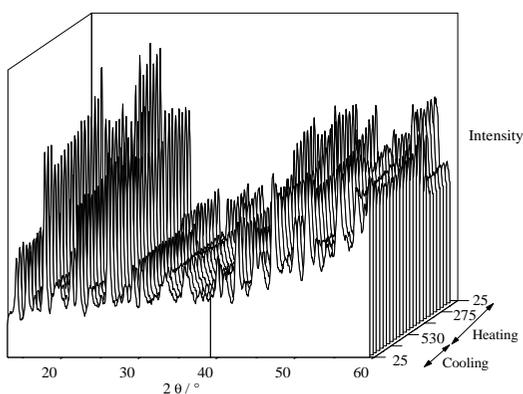
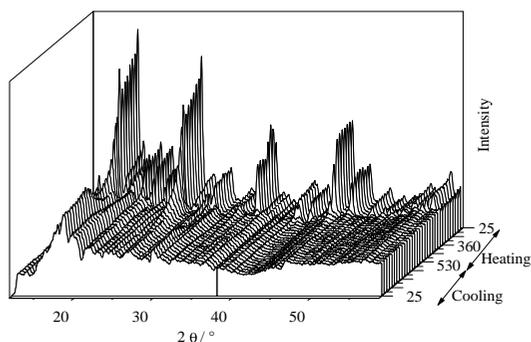
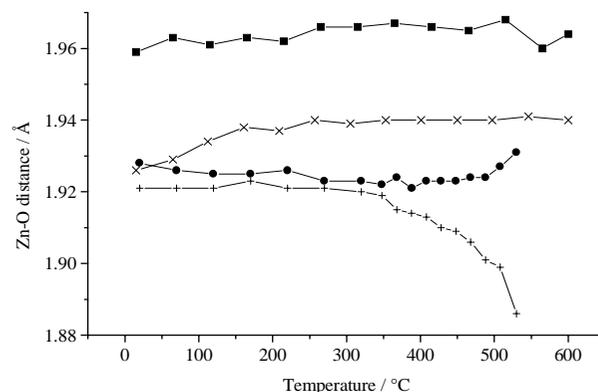
**Figure 1**

Figure 1. Stacked X-ray diffraction patterns of (top) ZnAPO-44 and (bottom) ZnAPSO-44 collected below the Zn K-edge during the heat treatment process

crystallinity is retained during the entire heat treatment process, it is known [Muncaster, 2000] that the structure directing organic template molecule starts to decompose in the temperature region of 350–400 °C. Although there was no tridymitic phase formation, similar to CoAlPO-44 [Barrett et al (1995)], the overall results are very similar to that observed for CoAPSO-44, that Si substitution in place of phosphorous and decrease in the amount of zinc stabilises the microporous structure.

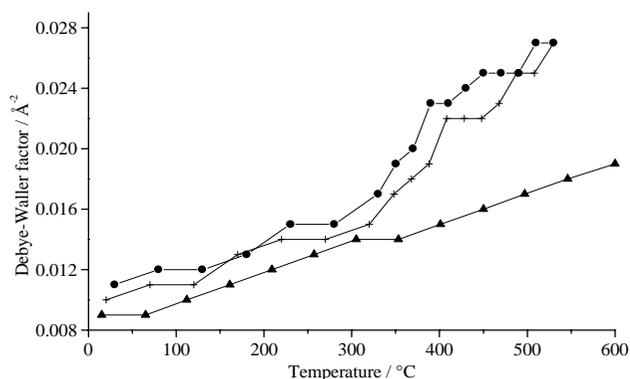
A detailed analysis of the Zn K-edge EXAFS data were carried out to understand the effect on the local structure around zinc in both the catalysts containing only zinc and the one containing both zinc and silicon. The variation in Debye-Waller factor, Zn-O distances for the two samples are shown in Figure 2 and 3. However, it is also known that EXAFS derived bond-distances for data collected at elevated temperatures are generally underestimated. In order to make sure the results are consistent, we measured both the EXAFS and diffraction data for ZnO and ZnAl₂O₄ under identical thermal conditions. The variations in the cell parameters are shown in Figure 4 which indeed show, as expected, that the lattice constants increase with temperature.

For both ZnO and ZnAl₂O₄, the EXAFS derived Zn-O distances did not vary much (well within the error limits of +0.02 Å), and the Debye-Waller factors showed the expected near-linear

**Figure 2**

Variation in Zn-O distances as a function of temperature

Key: + ZAPSO-44 (0.1 Zn, 0.3 Si); x ZnAl₂O₄; circles - ZAPO-44 (0.4 Zn), squares - ZnO.

**Figure 3**

Variation in Debye-Waller factor as a function of temperature. Key: + ZAPSO-44 (0.1 Zn, 0.3 Si); triangles - ZnAl₂O₄; circles ZAPO-44 (0.4 Zn).

variation as a function of temperature.

From the comparison of the Debye-Waller factor for the ZnAPSO-44 and ZnAPO-44 samples with the ZnAl₂O₄ standard, it is clear that both the catalyst materials showed increase in the static disorder, assuming the thermal contribution is similar to the standards. However, the most striking results are seen in the variation of the Zn-O distances. ZnAPO-44 showed a slight increase in the Zn-O distance, whereas the Zn-O distances of ZnAPSO-44 showed the opposite trend.

It is also interesting to note that the deviation from near-linearity in both Zn-O distances and the Debye-Waller factor are seen at temperatures above 375 °C. As noted before, this is the temperature at which the organic template starts to decompose.

Thus, our results show that for ZnAPO-44, when the open-framework structure collapses due to the removal of the organic template, there is a slight increase in the Zn-O distance. Also, due to the disordered (X-ray amorphous) nature of the solid formed, there is an increase in the static disorder component of the Debye-Waller factor. On the other hand, the stable ZnAPSO-44 showed a decrease in the Zn-O distance and an increase in the Debye-Waller factor. This may be readily explained by the formation of Brønsted acid sites.

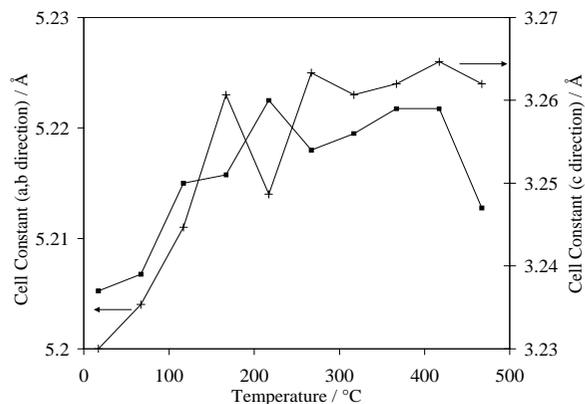


Figure 4
Variation in Cell parameters determined from X-ray diffraction data for the model compounds ZnO.

The loss of charge compensating organic template molecules result in the addition of a proton to one (see figure 5) of the bridging oxygen linking Zn^{2+} and P^{5+} . This type of Brønsted acidity is known to introduce a distortion to the tetrahedral geometry [Barrett et al 1996]. Both computational and experimental methods suggest the distorted geometry of this Brønsted acid site possesses three short bonds (generally shorter than the normal tetrahedral distance) and one longer bond. Thus, the decrease in Zn-O distance is likely to be due to the formation of the distorted tetrahedral site, which is also reflected in the increase in the static disorder. *In situ* FTIR spectra clearly support the above model for the formation of Brønsted acidity in the ZnAPSO-44 catalyst, and the lack of any hydroxyls in the collapsed ZnAPO-44 material (see Figure 5).

4. Conclusions

In summary, we have shown that the use of combined XAS/XRD can be used to understand the processes occurring during the calcination of ZnAPSO-44 catalysts. We have shown that the incorporation of both Si and Zn simultaneously increases the thermal stability of the materials produced as has been observed previously for incorporation of Co (Barrett *et al.*, 1995). Furthermore, by comparison with ZnAl_2O_4 and ZnO standards we are able to explain the structural modification seen by EXAFS during the activation of the catalysts.

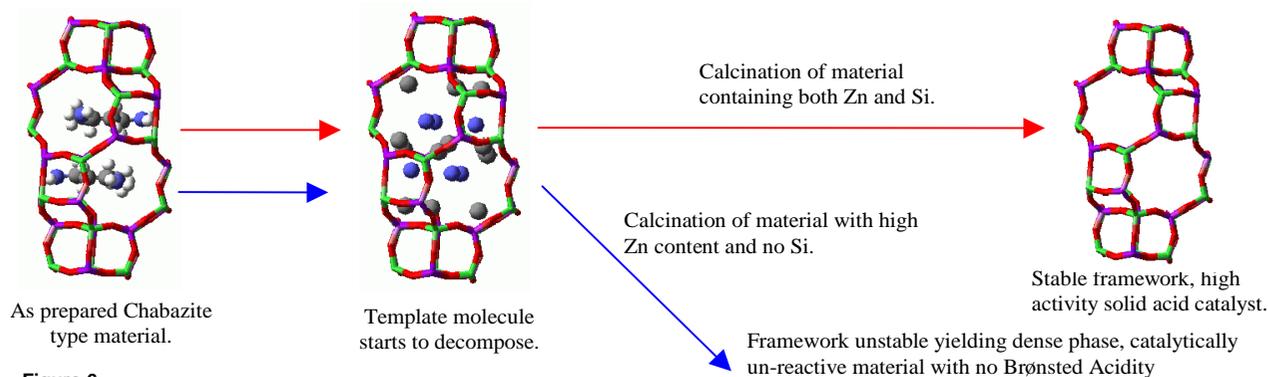


Figure 6
Computer graphic representation of the process of template is shown in this figure which summarises the process followed by the *in situ* combined XRD/QuEXAFS technique, decomposition and formation of either active catalyst or the dense phase

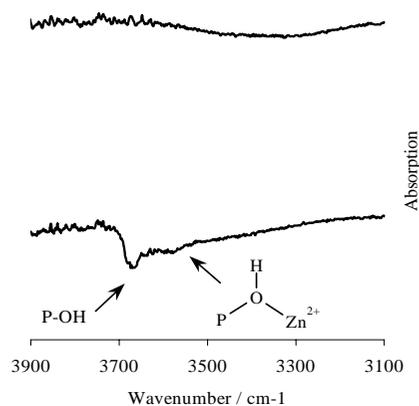


Figure 5
Fourier transform Infrared spectrum of the ZnAPO-44 and ZnAPSO-44. The hydroxyl sites are schematically shown in this figure. Key:- 0.4 Zn (top) and 0.1Zn (0.3Si) ZnAPSO-44 (bottom) materials immediately after calcination (*in situ*) in oxygen at 550 °C.

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