



	Experiment title: Catalysts at work: In-situ XAS and Powder diffraction studies of catalysts at real working conditions.	Experiment number: 01-02- 785
Beamline: BM01A	Date of experiment: from: 5/10/08 to: 8/10/08	Date of report: 22/1/09
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Report:

Unusual Negative Thermal Expansion Behaviour Of SAPO-34 Synthesised With And Without Hydrofluoric Acid

Studies of the behaviour of SAPO-34 under when heated have revealed negative thermal expansion behaviour. Negative thermal expansion is reasonably common in zeolitic framework materials¹ and has been observed for the pure silica form of chabazite (which has the same framework topology as SAPO-34) by Woodcock et al.² We have studied the thermal behaviour of two samples of SAPO-34, prepared by different synthetic routes with 5.5 and 8% silicon substituted for phosphorus, and one of AlPO-34 prepared by the hydrofluoric acid route.³

Time resolved powder X-ray diffraction (PXRD) data were collected on station BM01A of the Swiss-Norwegian Beamline.⁴ Samples were packed in 0.7mm quartz capillaries and mounted on the diffractometer with a Huber goniometer. Data were collected with a Mar 345 image plate detector at a wavelength of 0.7239980Å and a time resolution of 2 minutes per powder image. During the data collection the temperature was raised from room temperature to 900°C at a rate of 10°C per minute. The image plate data were converted into 2-dimensional PXRD patterns using FIT2D⁵ and the unit cell dimensions were obtained by Rietveld refinement against the rhombohedral chabazite framework model from the International Zeolite Association structure database with Al and P as the tetrahedral atoms.⁶ The AlPO-34 (a) and SAPO-34 (5.5% Si) (b) samples were prepared by hydrothermal synthesis in the presence of hydrofluoric acid (HF) with morpholine as structure directing agent while the SAPO-34 (8% Si) sample (c) was prepared without hydrofluoric acid, using tetraethylammonium hydroxide as template.

Plots of the variation against temperature of the unit cell axes and volume are given in figure 1. The behaviour of c is clearly different to that of the two samples prepared by the hydrofluoric acid route. The

initial stages of heating for **c** show an expansion in all unit cell directions as the structure is dehydrated, The *c*-axis reaches its maximum value at 200°C while the maximum value of cell volume and *a* is reached at 323.5°C. The maximum value of *a* and volume for samples **1** and **2** is found at room temperature however there is a short phase of increase close to the dehydration temperature. The maximum value of *c* is at 148.5°C.

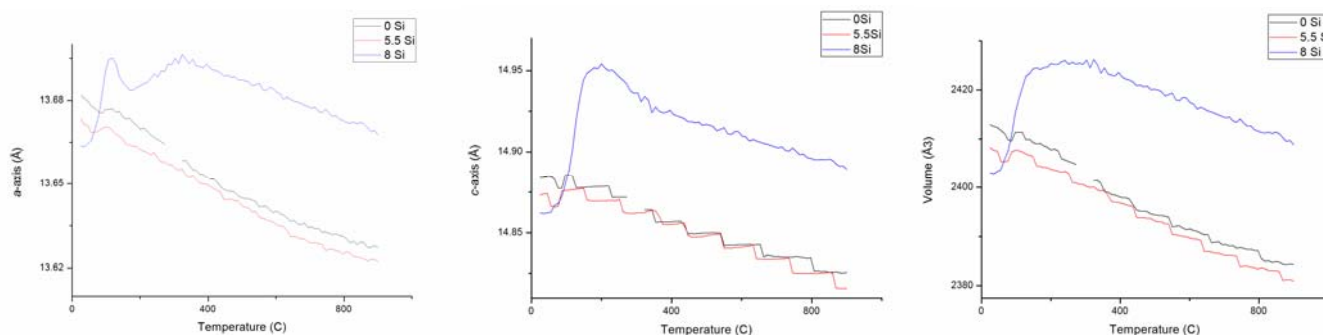


Figure 1. Plots of (from left to right) the *a* and *c*-axes and unit cell volume of three samples of AlPO/SAPO-34 against temperature for the range from room temperature to 900°C.

The hydrated structures of AlPO-34 prepared with and without HF are known to be different with the HF material transforming to a triclinic structure on hydration⁷ and the HF free material remaining rhombohedral.⁸ The fit we achieved using the rhombohedral framework model however does appear to give reliable peak positions even in the region where some triclinic peaks are visible (e.g. the initial 1 1 0 peak; figure 2). We therefore believe the unit cells to be reliable.

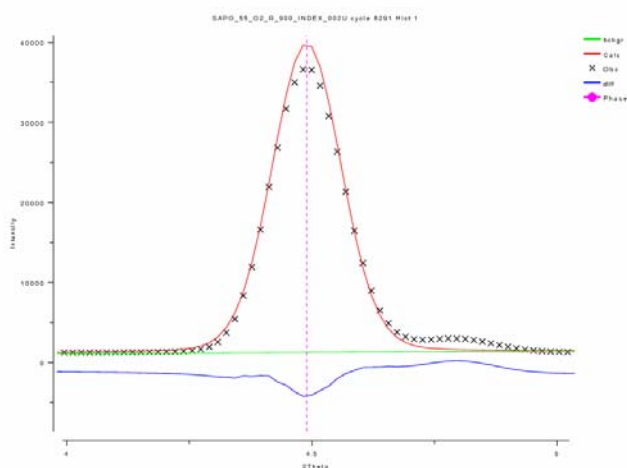


Figure 2. Rietveld plot of the 110 peak of sample **b** (5.5% Si, synthesised with HF). The shoulder to the right of the main peak is due to the triclinic hydrated structure and is not fitted by the model however the position of the dotted peak marker line is clearly correct.

The variations in the unit cell parameters between 25 and 900°C are shown in table 1. The *c*-axis variations between the maximum and 900°C values are similar for all three materials and larger than the corresponding values for *a*-axis variation. The *a*-axis variation for sample **c** is smaller than for **a** and **b** and this is reflected in the maximum to 900°C volume changes.

Dehydration of the samples is the driver behind the behaviour of the samples at lower temperatures. Plotting the residual electron density (principally due to water content) in Fourier maps calculated for sample **3** shows that the negative thermal expansion of the *a*-axis sets in once the residual electron density hits a value of around 0.6 electrons per Å³ - close to the minimum value of residual electron density. The oscillation in the value of the electron density at this point is probably due to the structural changes taking place as the last water is removed (figure 3).

	a-axis (Å)			c-axis (Å)			Volume (Å ³)		
	a	b	c	a	b	c	a	b	c
RT	13.681 8	13.6735	13.6638	14.8841	14.8732	14.8622	2412.8 8	2408.2	2403
Max	13.681 8	13.6735	13.6951	14.8886	14.8769	14.9543	2412.8 8	2408.2	2426.2
900°C	13.627 3	13.6222	13.6678	14.8256	14.8159	14.8892	2384.9 7	2380.97	2408.8
Max-RT	0	0	0.0313	0.0045	0.0037	0.0921	0	0	23.2
RT-900°C	0.0545	0.0513	-0.004	0.0585	0.0573	-0.027	27.91	27.23	-5.8
Max-900°C	0.0545	0.0513	0.0273	0.063	0.061	0.0651	27.91	27.23	17.4

Table 1. Unit cell parameters at room temperature, maximum value and 900°C along with differences.

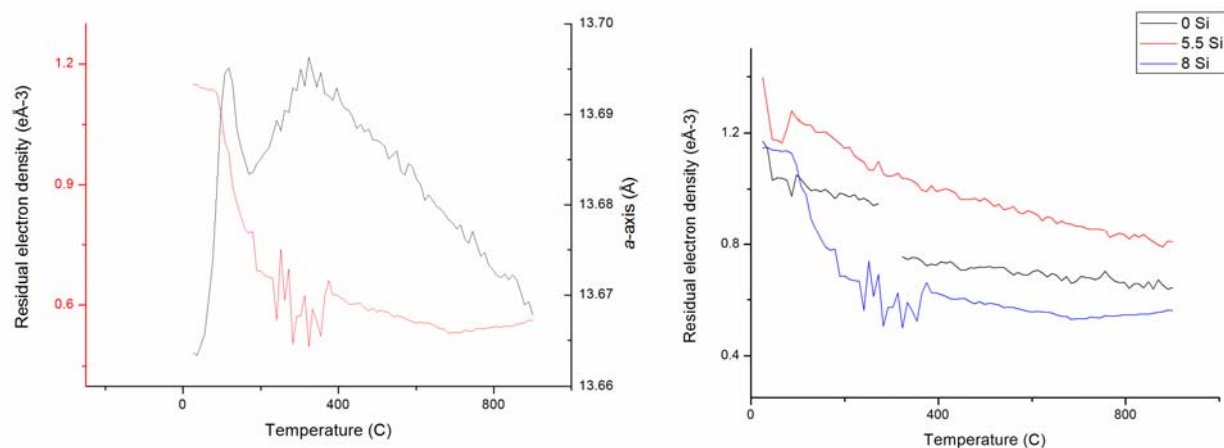


Figure 3. Plots of a -axis change and residual electron density for sample 3 (8% Si, no HF in synthesis), left. Plots of residual electron density for all three samples, right.

Comparing the residual electron density plots for all three samples again shows that the pattern for samples synthesised with and without HF is, as would be expected from the data above, different, however the overall electron density change between 25 and 900°C is roughly the same for all samples (between 0.5 and 0.6 eÅ⁻³) indicating that about the same amount of electron density is lost for all samples. The step change in electron density due to loss of water takes place earlier in the samples prepared with HF and probably causes the unusual a -axis behaviour in the sample prepared without.

To conclude, we have observed slightly different patterns of negative thermal expansion in samples of AIPO and SAPO-34 prepared with and without HF. The unusual behaviour occurs at low temperatures and seems to be related to differences in the binding of water. It is likely that this phenomenon is related to the fact that AIPO-34 prepared in triclinic form with HF can revert to triclinic symmetry on hydration.⁷ Samples 1 and 2 in this study appear not to have been fully converted to the triclinic form before heating though triclinic features are still visible in the powder patterns at 25°C- the fact that difference in behaviour can still be observed in the in situ data show the importance of this change.

References

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