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# Synthesis of high silicon content $SAPO_4$-5 using anionic surfactants in a hexanol/aqueous two phase media

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***Received (in Cambridge, UK) 30th October 2001, Accepted 6th December 2001***

***First published as an Advance Article on the web 10th January 2002***

**High silicon content $SAPO_4$-5 (up to 0.511 atoms per unit cell) has been synthesised, using sodium 3-bromopropanesulfonate, sodium 1-butanesulfonate, sodium naphthalene-1-sulfonate or sodium *n*-decyl sulfate as surfactants; the $SiO_2$ in the reaction gels ranged up to 3.0 (molar ratio), silicon incorporation was confirmed by XRD, XRF, TG-DTA, FT-IR and SEM techniques.**

Industrially important silicoaluminophosphates ($SAPO_4$s) have been widely used as acidic catalysts[1] since their first synthesis in the 1982.[2] For reactions requiring highly acidic catalysts, it is advantageous to synthesise $SAPO_4$s with a high silicon content as the acidic sites are located both on dispersed silicon ions[3] and the edge of silicon islands.[4] However, the narrow range of the initial $SiO_2$ concentration[5] in the reaction gel has limited the silicon content in the final product. It is important therefore to broaden the $SiO_2$ concentration in the reaction gel when synthesising siliceous $SAPO_4$s.

Hexanol/aqueous two-phase media have been found to slow down the delivery of silicon from the alcohol media to the aqueous media in the presence of a surfactant,[6] which in turn affects the dispersion of silicon in the solid $SAPO_4$s.[7]

This work approaches the synthesis of siliceous $SAPO_4$-5 by broadening the $SiO_2$ concentration in the reaction gel ($Si_R$) using the presence of sodium 3-bromopropanesulfonate (Sa), sodium 1-butanesulfonate (Sb), sodium naphthalene-1-sulfonate (Sc) or sodium *n*-decyl sulfate (Sd) in the two-phase media.

Crystalline $SAPO_4$-5 was synthesised from the gel molar composition: $n\ SiO_2:1\ Al_2O_3:1\ P_2O_5:40\ H_2O:4$ hexanol: 0.07–0.1 sulfonate: 1 TEA; ($n$ = 0.2–3.0).

To prepare the alcohol phase, aluminium isopropoxide (Aldrich, 98%), tetraethyl orthosilicate (Aldrich, 98%) and sulfonate or sulfate (Lancaster, 99%) were added into hexanol (Aldrich, 98%) while stirring, and the mixture was stirred until it reached homogeneity. To prepare the aqueous phase, TEA and orthophosphoric acid (May & Baker Ltd, 90%) were added to pure water while stirring. The two phases were then stirred for a further hour before they were mixed together. The mixture was then stirred for a further hour to form the reaction gel. Finally, the gel was introduced into Teflon lined reaction vessels and incubated in a 423 K oven. Gel samples were taken at 24 h intervals, washed repeatedly with pure water and dried at 313 K.

X-Ray analysis confirms a typical crystallinity at 97.4% and purity of the $SAPO_4$-5; the XRD patterns of as-synthesised $SAPO_4$-5 material matched the $AlPO_4$-5 ICDD standard pattern number 41-44, as shown in the graphical abstract. They also agree with reported finding,[8] which confirms isomorphous substitution of silicon into the framework. The samples were X-rayed again after calcination showing that the material is thermally stable at 900 °C. TG–DTA analysis shows an average 11% water loss at around 373 K, 5% TEA loss at around 673 K and 3% sulfonate loss at 823 K to 873 K. This indicated that sulfonates had attached to the surface of the $SAPO_4$-5 more strongly than TEA. The average total loss was higher than the loss from samples synthesised without using sulfonate. FT-IR results of synthesised $AlPO_4$-5 and as-synthesised $SAPO_4$-5 match the reference data of $AlPO_4$-5s,[9] except that the FT-IR pattern of as-synthesised $SAPO_4$-5 shows a peak at 800 $cm^{-1}$ shown by framework $SiO_4$,[10] providing further evidence of silicon incorporation into the AFI framework (Fig. 1). The unit cell composition were calculated from XRF data, and confirms the silicon content in the as-synthesised sample ($Si_S$), Table 1. SEM micrographs (Fig. 2) show the size and morphology of the as-synthesised samples. Hexagons and 'flaked' groups of hexagons over-laid on each other to form a spherical shape with a hole at each pole indicates that the particles could be empty in the centre. All particles were uniform, having a average diameter of 30–40 μm. In some over-run samples, there were a few cylinder shapes.

Crystalline $SAPO_4$-5 was successfully synthesised with $Si_R$ up to 2.6 mol in the presence of sulfonates and sulfate (Table 1). In the case of sulfonate Sa, the Si content in the material increased steadily to its highest value of 0.511 atoms per unit cell, while $Si_R$ reached 2.2 mol. The Si content per unit cell of samples from the gels with $Si_R \geqslant 2.6$ mol was not calculated due to their low crystallinity.

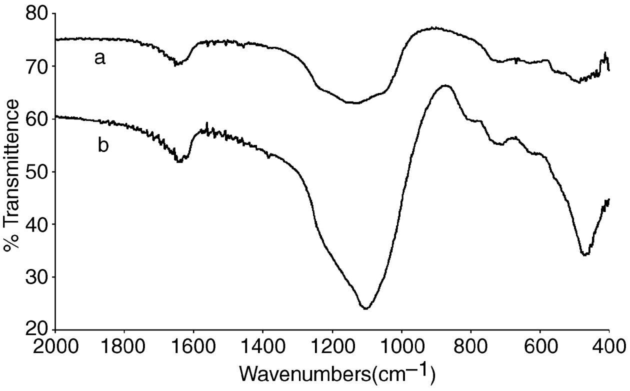

**Fig. 1** FT-IR pattern of as-synthesised $SAPO_4$-5: (a) synthesised $AlPO_4$-5 as reference; (b) as-synthesised $SAPO_4$-5 from reaction gel with $SiO_2$ = 2.4).

**Table 1** Gel and sample compositions

| $Si_R$ | Unit cell composition ($Al_xP_ySi_zO_2$) $x$ | $y$ | $z$ | Crystallinity (%) |
|---|---|---|---|---|
| 0.2 | 0.479 | 0.443 | 0.078 | 97.4 |
| 0.4 | 0.483 | 0.370 | 0.146 | 98.0 |
| 0.6 | 0.438 | 0.323 | 0.239 | 96.5 |
| 0.8 | 0.418 | 0.341 | 0.241 | 95.8 |
| 1.0 | 0.435 | 0.350 | 0.215 | 97.2 |
| 1.2 | 0.383 | 0.329 | 0.289 | 93.1 |
| 1.4 | 0.400 | 0.342 | 0.259 | 94.8 |
| 1.6 | 0.326 | 0.298 | 0.376 | 90.7 |
| 1.8 | 0.330 | 0.281 | 0.389 | 98.5 |
| 2.0 | 0.333 | 0.288 | 0.379 | 97.3 |
| 2.2 | 0.246 | 0.243 | 0.511 | 95.4 |
| 2.4 | 0.330 | 0.244 | 0.446 | 90.0 |
| 2.6–3.0 | — | — | — | 50–30 |

DOI: 10.1039/b109906j

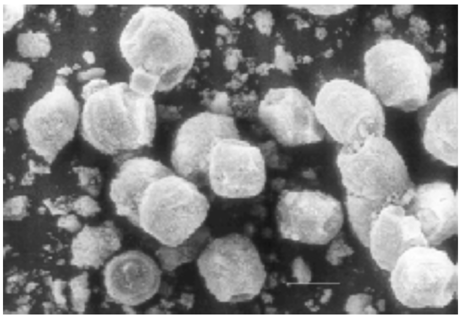

**Fig. 2** SEM image of the as-synthesised $SAPO_4$-5 (scale bar = 30 μm).

Among the four different sulfonates, Sa produced the broadest gel content range up to 3.0 mol, as well as the highest $Si_S$ (0.511) (Table 1). Sulfonate Sa made the synthesis with $Si_R$ = 3.0 mol possible, while $Si_R \leqslant 2.4$ gave the most crystalline samples. Therefore Sa proved to be the most efficient sulfonate being used in the present study.

In the synthesis using sulfonates Sb, Sc and sulfate Sd, crystallisation behaviour was similar to the synthesis using sulfonate Sa with $Si_R$ from 0.2 to 2.0 mol, but sulfonates Sb, Sc and Sd failed to produce $Si_S$ higher than 0.4 atoms per unit cell before giving poorly crystalline material. The different structures of the sulfonates and sulfate did not significantly affect the morphology of the products, but they did produce different levels of $Si_R$ thus producing different levels of $Si_S$, given in Table 2. This might be caused by the different emulsion abilities between the two phases due to the different sulfonate structures. The anionic characteristic of sulfonates did not affect silicon incorporation although the reaction is believed to be favoured by protons.[11]

**Table 2** Comparison of the four sulfonates

| Surfactant | Max $Si_R$/ mol | Max $Si_S$/ Atoms (unit cell)$^{-1}$ |
|---|---|---|
| Sa | 2.2 | 0.511 |
| Sb | 2.0 | 0.373 |
| Sc | 1.8 | 0.319 |
| Sd | 1.6 | 0.327 |

## Notes and references

1 L. H. Gielgens, I. H. E. Veenstra, V. Ponec, M. J. Haanepen and J. H. C. van Hoof, *Catal. Lett.*, 1995, **32**,195.

2 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.

3 G. Sastre, D. W. Lewis and C. R. A. Catlow, *J. Phys. Chem. B*, 1997, **101**, 5249.

4 M. Brend, M. Derewinski, A. Lamy and D. Barthomeuf, in *New Frontiers in Catalysis, 10th Int, Congr. Catal.*, ed. L. Guczi, F. Solymosi and P. Tetenyi, Akaemiai Kiado, Budapest, Hungary, 1993, p. 409.

5 J. Das, C. V. Satyanaryana and D. K. Chakrabarty, *J. Chem. Soc., Faraday Trans.*, 1992, **88**(21), 3255.

6 M. Montoya-Urbina, D. Cardoso, J. Perez-Pariente, E. Sastre, T. Blasco and V. Fornes, *J. Catal.*, 1998, **173**, 501.

7 K. G. Strohmaier and D. E. W. Vaughan, *World Pat.*, WO 99/61372, 1999.

8 http://www.zeolites.ethz.ch/zeolites/XRDPatterns/AFI

9 R. Szostak, *Handbook of Molecular Sieves*, Van-Nostrand Reinhold, New York, 1992, p. 10.

10 K. Nakamoto, *Infrared and Raman spectra of Inorgainc and Coordination Compounds, Part A, Theory and Applications in Inorganic Chemistry*, John Wiley and Sons Inc, New York, 5th edn., 1997, p. 199.

11 G. Sastre, D. W. Lewis and R. A. Catlow, *J. Phys. Chem.*, 1996, **100**, 6722.