

A New As³⁺-Silicate Molecular Sieve with MFI Structure

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New arsenosilicate molecular sieves with MFI topology ([As³⁺]MFI) efficiently crystallise at relatively low temperature (*ca.* 85 °C) in 1–2 days (faster than the As-free pure silicalite-1) and exhibit an increased unit cell volume, significant ion-exchange capacity and catalytic activity in acid catalysed *n*-hexane cracking.

Among microporous solids, silica based molecular sieves have been extensively studied mainly due to their remarkable catalytic properties in various reactions. A number of metal ions, particularly transition metals, of type M³⁺ (*e.g.* Al, Ga, Fe and Cr) and M⁴⁺ (*e.g.* Ti, V and Sn) with different catalytic characteristics, can be incorporated in silica based zeolitic network, particularly of the MFI type.¹ In phosphate based molecular sieves (*e.g.* aluminophosphates,^{2,3} beryll/zincophosphates,⁴) various metal and non-metal ions, can be incorporated. Recently, Gier and Stucky,⁴ reported the synthesis of beryll/zinc arsenate analogues of different zeolites *e.g.* RHO, A, X. A remarkable feature of the synthesis of these Be/Zn-arsenates is their low temperature (*ca.* 70 °C) crystallization in a short time (2–3 days). A microporous crystalline aluminosilicate⁵ has also been reported. However, the synthesis of an As³⁺-containing silica based molecular sieve has not yet been reported. In all other types of As-containing microporous materials, As was in a pentavalent (As⁵⁺) state.

Here, we report a highly efficient synthesis of first As³⁺-silicate analogue of the MFI zeolite at a relatively low temperature (85 °C) in 1–2 days, depending upon As content. A remarkable feature of these arseno-silicate molecular sieves is that they can be crystallized faster than the As-free silicalite-1 (Table 1). Interestingly, the crystallization of silicalite-1, compared to all other high silica zeolites, is commonly known to be fastest among all high silica molecular sieves.

In a typical synthesis, tetraethyl ortho silicate (Aldrich, USA) was hydrolysed with tetrapropyl ammonium hydroxide solution (TPAOH, 20 mass% aq., Aldrich) with stirring for 1 h. The required amount of As₂O₃ was dissolved in dilute aqueous NaOH solution then added very slowly to the hydrolysed silicate gel. The clear liquid obtained was stirred for another 1 h, then more water was added. The pH of the final gel ranged from 11.5 to 12.5 depending upon the As content in the gel. The solution was then put in polypropylene bottle and heated at 85 °C for 1–2 days. The molar compositions of the starting mixture was SiO₂:xAs₂O₃:0.1 Na₂O:0.4 TPAOH:30 H₂O [*x* = 0.05 (A), 0.025 (B), 0.0125 (C) and 0.0 (Silicalite-1, D)]. After crystallization the product was removed, washed thoroughly with hot water, dried at 373 K and calcined at 500 °C for 16 h in flowing air. The product yield was *ca.* 80% (on the basis of SiO₂).[†] The Na form of the zeolite thus obtained after calcination was treated with 1 mol dm⁻³ ammonium acetate solution at 80 °C for 4 h followed by calcination in flowing air

at 500 °C for 16 h to obtain the H form. These samples were characterised through chemical analysis (ICP), XRD, IR and UV-VIS spectroscopy, SEM, ion exchange and catalytic studies.

It is clear from Table 1 that the hydrothermal synthesis of [As³⁺]-MFI can be carried out at significantly lower temperatures than those required for synthesizing other metal substituted MFI silicates as well as pure silica polymorph (silicalite-1). This is probably the first report of the synthesis of high silica zeolites at as low as 85 °C, in less than 2 days. However, the crystallization can be completed in 18 h at 90 °C. Pure silicalite-1 takes about 3 days at 90 °C. This may be due to greater solubility of the As³⁺ under hydrothermal conditions. A common observation is that the incorporation of a hetero-metal ion in high silica zeolites is a difficult process.⁶ Here it may be pertinent to mention that after ammonium acetate treatment, mentioned above, no As was found in the filtrate indicating that As is firmly incorporated in the zeolitic framework. Since As₂O₃ is freely soluble under hydrothermal conditions, it is unlikely that crystalline solid will contain occluded As-oxides.

The XRD profiles of [As³⁺]-MFI samples (A–C) were typical of MFI topology and matched with that of As-free silicalite-1. An increase in the unit cell volume was observed with the increase in As content in the [As³⁺]-MFI samples (Table 1). SEM of the as-synthesized samples A–D, recorded by JEOLJSM 5200, exhibited very small (0.3–0.5 μm) cuboid shaped crystallites. No amorphous material was observed. An IR absorption (shoulder) at *ca.* 960 cm⁻¹ (in addition to all other bands exhibited by As-free silicalite-1) was observed in the IR spectra of samples A–C. Both, As-free and As impregnated silicalite-1 do not exhibit this band. Similar observations were made in the case of other metallosilicate molecular sieves.^{7–9} This band is commonly attributed to Si–O–X stretching vibrations (where X is the heteroatom). UV-VIS spectra of the calcined samples (A–C) show a charge transfer band at around 215 nm indicating presence of As in T_d coordination expectedly in the silicalite-1 lattice. The absence of an absorption at 330 nm indicates the absence of clustered As-oxides.

As³⁺-silicate samples (A–C) exhibited considerable cation exchange capacity (K/As Table 1). The cation exchange capacity in the zeolites originates from the presence of isolated M³⁺ ions in regular T_d silicate framework, hence these values are considered a semiquantitative proof for the incorporation of

Table 1 Physicochemical properties of MFI type arsenosilicate molecular sieves

Sample ^a	Si/As mol ratio		Ion exchange capacity ^b K/As	Crystallation time /h ^a	BET surface area /m ² g ⁻¹	Unit cell volume /Å ³
	Gel	Product				
[As]-MFI A	10	15	0.82	24	512	5360
[As]-MFI B	20	27	0.80	32	499	5354
[As]-MFI C	40	50	0.83	46	497	5349
Silicalite-1 D	∞	—	—	76	439	5339

^a *T* = 85 °C, static conditions. ^b Calcined, organic free samples A–C were subjected to ion exchange with a 1 mol dm⁻³ solution of KCl at 80 °C for 3 h. This treatment was repeated twice. The samples were then recovered, washed thoroughly and analysed for K and As.

M³⁺ ions in the framework.¹ The quite high values for K/As molar ratio in the our sample (Table 1) clearly suggest the incorporation of As³⁺ in MFI structure. Further, these As-silicates were quite active in Bronsted acid catalysed *n*-hexane cracking. For example, sample A exhibited 25% *n*-hexane conversion at 350 °C (fixed bed quartz reactor with 10 mm i.d., 1 g binder free catalyst, feed rate of *n*-hexane: 4 ml h⁻¹). Under similar reaction conditions As-free silicalite-1 and ZSM-5 (Si/Al = 20) catalyse *ca.* 2 and 32% *n*-hexane conversion, respectively. These results show that the Bronsted acid sites are present on As-silicates, the strength of which is lower than that of Al-ZSM-5.

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† Although the toxicity of these new materials is not known, they were handled with the precautions required for toxic compounds.

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