Low temperature, efficient synthesis of new As(V)-silicate molecular sieves with MFI topology and their catalytic properties in oxidation reactions

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New MFI type arseno-silicate molecular sieves (As(V)-MFI), synthesized for the first time, can be crystallized at lower temperature (70–90°C) in 1–3 days under hydrothermal conditions. Interestingly, these As(V)-MFI molecular sieves can be synthesized even faster than the As-free silicalite-1 under identical conditions. Further, the crystallization becomes faster with the increase in As content of the reaction mixture, contrary to the observations made on all the other high silica molecular sieves, so far. These microporous As(V)-silicates exhibit significant catalytic activity in (i) phenol hydroxylation using 30% aq. H_2O_2 (ca. 55% H_2O_2 efficiency) and (ii) oxidative dehydrogenation of 2-butanol and benzyl alcohol using air under fixed bed vapor phase reaction conditions exhibiting ca. 75–85% selectivity towards 2-butanone and benzaldehyde + benzoic acid, respectively.

Keywords: As(V)-silicate molecular sieves; MFI type As zeolite; catalyst; oxidation catalysis; phenol hydroxylation with H_2O_2; oxidative dehydrogenation; alcohols; air or O_2

1. Introduction

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 of the type M^{3+} (like Al, Ga, Fe, Cr, etc.) and M^{4+} (like Ti, V, Sn, etc.) with different catalytic characteristics, could be incorporated in silica based zeolitic network [1–3]. Recently, Gier and Stucky [4] have reported the synthesis of beryllo/zinco-arsenate (As(V)) analogues of different zeolites like RHO, A, X, etc. A remarkable feature of the synthesis of these Be/Zn-arsenates was their low temperature (~ 70°C) crystallization in few days (2–3 days) time. Generally, these non-metal based molecular sieves crystallize at lower temperature (below 100°C) while metallo-silicate molecular sieves (particularly high silica ones) require

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higher temperature. This difference is attributed to higher solubility of the former under hydrothermal synthesis conditions [4]. Although As(V) could be incorporated in alumino-arseno-phosphates [1] and alumino-arsenates [5], As(V)-silicate molecular sieves have not been reported, so far, in the literature.

Now, we report the highly efficient, low temperature (75 ± 15°C) synthesis of the first arseno-silicate[#1] analogues of MFI zeolite which can be prepared in few hours to few days time depending upon temperature. The use of these new materials as oxidation catalysts was explored in phenol hydroxylation using H_2O_2 in a liquid phase batch reactor and oxidative dehydrogenation of 2-butanol and benzyl alcohol using molecular oxygen (air) under fixed bed vapor phase conditions.

2. Experimental

In a typical synthesis, tetraethyl ortho silicate (Aldrich, USA) was hydrolyzed with a TPAOH (20%, Aldrich) solution under stirring for 1 h. Then an aqueous solution of di-sodium hydrogen arsenate ($Na_2HAsO_4 \cdot 7H_2O$; Loba, India) was added very slowly into it. The clear liquid, thus obtained, was stirred for another 1 h, then the remaining quantity of water was added. The pH of the final gel ranged between 11 and 12.5 depending upon the As content in the gel. Then the solution was put in a polypropylene bottle and heated in the temperature range 60–90°C. After complete 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 75–80% (on the basis of SiO_2). Four such As(V)S-1 samples with Si/As input molar ratios 15, 20, 40 and 80 were prepared (samples a, b, c and d respectively) and characterized by X-ray powder diffraction (XRD), IR, UV-VIS, SEM spectroscopic techniques, ion exchange studies and chemical analysis by ICP.

3. Results and discussion

3.1. SYNTHESIS

In the hydrothermal synthesis of arseno-silicates, the molar compositions of the reaction mixture were: $SiO_2 : xAs_2O_5 : 2xNa_2O : 0.4TPAOH : 30H_2O$ ($x = 0.067$–0, and TPAOH is the organic template tetrapropyl ammonium hydroxide). These materials can be prepared from reaction mixtures at much lower temperature than 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 a temperature as low as 70°C within 66 h. How-

[#1] Although the toxicity of these new materials is not known presently, all the precautions were taken while handling these materials considering them as obnoxious.

Table 1
Physico-chemical properties of AS-1

Sample	Si/As mole ratio		Cryst. time[a] (h)	BET surface area ($m^2 g^{-1}$)	Unit cell volume ($Å^3$)
	gel	product			
As(V)S-1a	15	37	18	488	5352
As(V)S-1b	20	44	26	483	5349
As(V)S-1c	40	72	36	472	5346
As(V)S-1d	80	145	44	460	5342
As(V)S-1e[b]	20	84	03	449	5345
silicalite-1	∞	–	66	439	5340

[a] Temp. = 85°C, static conditions (under stirring/agitation, crystallization becomes slightly faster).
[b] Synthesis temperature = 170°C.

ever, the crystallization can be completed even in 18 h at 80°C or in 8 h at 90°C. A remarkable feature of these arseno-silicate molecular sieves is that they can be crystallized faster than even As-free silicalite-1 (table 1). Pure silicalite-1 takes about 4 days at 90°C. Interestingly, the crystallization of silicalite-1, compared to all other high silica zeolites, is known to be the fastest. Further, the crystallization becomes faster with the increase in As(V) content in the gel, i.e. decrease in Si/As molar ratio. These observations are contrary to the common experience in the synthesis of all other high silica metallo-silicates, where the incorporation of hetero metal ions (vis-a-vis silicate ions) is relatively a difficult process [1,6]. This may be due to (i) greater solubilities of the As(V) under hydrothermal conditions [4] and (ii) an increased charge/ionic radius ratio of As^{5+} (10.6) compared to that of Si^{4+} (9.7). Apart from the solubility and charge/radius ratio, other factors like pH, concentration of alkali metal and template, dilution etc. affect the crystallization of these arseno-silicates. Since As(V)-oxides are soluble under hydrothermal conditions, it is unlikely that the crystalline solid will contain occluded As-oxides. The uptake of As(V) from the reaction mixture into solid material was nearly 50% (table 1, entries 1–4). The incorporation of As(V) in the crystalline solid reduced further to nearly 25% at higher temperature (table 1, entry 5). Higher solubility of As(V) at higher temperature may retard its uptake from solution.

3.2. CHARACTERIZATION

The XRD profiles of As(V)S-1 samples matched with that of As-free silicalite-1. The crystallinity of As(V)-silicate samples was ca. 95–97% of fully crystalline As-free silicalite-1. The crystallinity was calculated on the basis of integrated area of the peaks between $2\theta = 22°$ and 25°. However, slight increase in the unit cell volume was observed, as expected due to the incorporation of As(V) with ionic radius 46 pm in the silicate (the ionic radius of Si(IV) is 41 pm) network with the increase

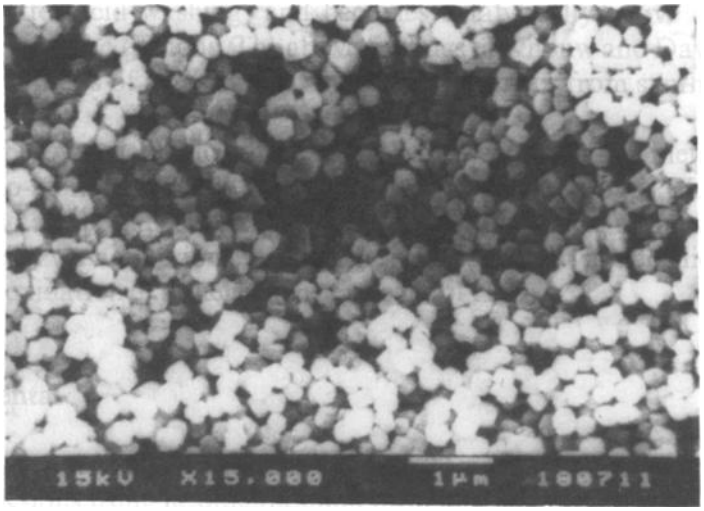


Fig. 1. Scanning electron micrograph of sample As(V)S-1b (as synthesized).

in As content in the arseno-silicates (table 1). Scanning electron micrographs (SEM) of the as-synthesized sample As(V)S-1a, recorded by JEOL JSM 5200, exhibited very small (0.2–0.3 μm) cuboid shaped crystallites (fig. 1). No amorphous material was observed. The UV-VIS spectra of the calcined samples of As(V)-silicates show a charge transfer band at around 215 nm indicating the presence of As in T_d coordination expectedly in the silicalite-1 lattice (fig. 2). The absence of a

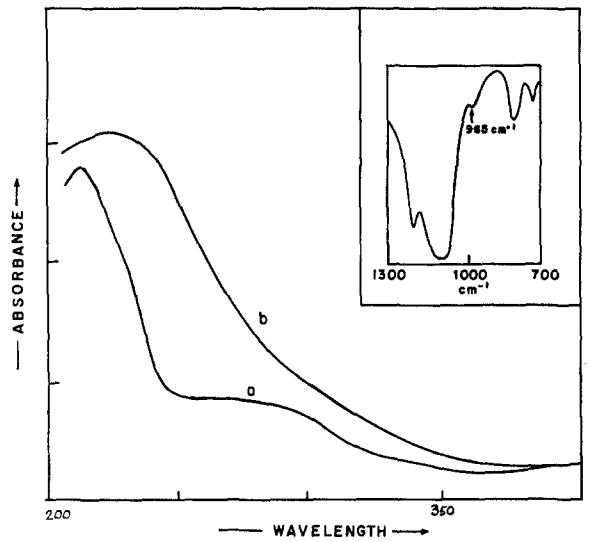
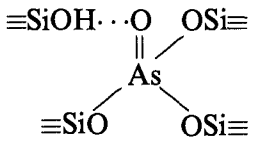


Fig. 2. UV-VIS spectrum of sample As(V)S-1b (calcined), inset: IR spectrum (framework region) of the same sample.

significant absorption at 330 nm indicates the absence of any appreciable amount of arsenic oxide. However, a small band at around 280–300 nm may be due to some occluded well dispersed As(V) oxide. However, this broad band may also be due to coordination of water to As (V) with expanded (> 4) coordination number. A small IR absorption band at around 960 cm^{-1}, in addition to all other bands in the framework region exhibited by As-free silicalite-1, was observed after ammonium acetate treatment and subsequent calcination of the samples (inset in fig. 2). As-free and As-impregnated silicalite-1 do not exhibit this band. Similar observations are made in the case of titanium and vanadium silicates (TS-1, TS-2, Ti-ZSM-48, VS-1, VS-2, V-NCL-1, etc. [2,7]. This band is commonly attributed to Si–O–X stretching vibrations (where X is a certain hetero atom like Ti, V, Sn, As, etc.). The XPS analyses of As(V)S-1 (samples a–d) show a strong peak in the range of BE = 159–160 eV corresponding to As(V) [8].

Since XPS spectra of samples a–d confirmed the presence of As(V) species we were tempted to find out whether As(V)-silicates exhibit any anion exchange capacity. Interestingly, no significant anion exchange capacity ($Cl^- \rightleftharpoons OH^-$) was observed, suggesting that As(V) may not be occupying regular corner sharing T_d positions in the MFI silicate network. Instead, it is likely that these As(V) species may be incorporated as species I:



Species I

Similar species have been suggested for V^{5+} in MFI/MEL type vanadium-silicates, VS-1/VS-2 [9]. This hypothesis is further supported by the hydroxyl region IR spectrum of As(V)S-1b sample (fig. 3) exhibiting (i) a strong absorption at 3741 cm^{-1} due to silanol groups, (ii) a weak shoulder at about 3714 cm^{-1}, probably due to silanols in the vicinity of As(V) and (iii) a very broad, weak absorption centered around 3646 cm^{-1}, which may be due to some hydrogen bonding between Si–O–H and As=O moiety in the proposed species I. A similar explanation has been reported for similar absorptions observed in pentasil type Ti- and V-silicates [10,11].

3.3. CATALYSIS

The samples a–d were found to be quite active in the hydroxylation of phenol using dilute (30 wt%, aq.) H_2O_2 (table 2). The catechol-to-hydroquinone ratio ranges between 1.35 and 1.5 (for phenol/H_2O_2 ratio = 3). MFI type Ti- and V-silicates also exhibit similar product distribution [7,9]. The H_2O_2 selectivity exhibited by As-silicate-1 is less than that reported for TS-1. This may be due to the

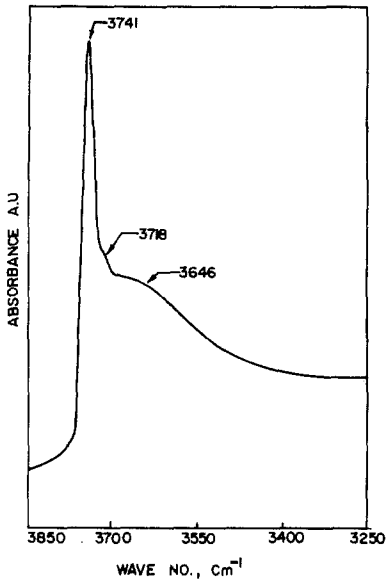


Fig. 3. FTIR (Nicolet, 60 SXB) spectrum (hydroxyl region) of As(V)S-1b obtained using self-supported wafer technique. The sample was evacuated at 673 K for 3 h under vacuum (10^{-6} Torr) in an all-silica home made cell, then cooled to 323 K before collecting the spectrum with 2 cm^{-1} resolution and averaged over 500 scans.

higher redox potential of As^{5+}/As^{3+} (0.55 eV, higher potential facilitates H_2O_2 decomposition) compared to that of Ti^{4+}/Ti^{3+} (0.06 eV). For the same reason, vanadium-silicates (redox potential for V^{5+}/V^{4+} = 1.0 eV) also exhibit lower H_2O_2 selectivity compared to that exhibited by Ti-silicate analogues [9].

Table 2
Hydroxylation of phenol over As(V)S-1 [a]

Sample	Phenol/H_2O_2 mole ratio	Phenol conv. (mol%)	H_2O_2 sel (%) [b]	Product selectivity (%)		CAT/HQ
				HQ	CAT	
As(V)S-1a	3	17.2	52.0	39.6	60.4	1.52
As(V)S-1b	3	16.8	51.0	40.1	59.9	1.49
As(V)S-1b	2	25.4	51.0	37.4	62.6	1.67
As(V)S-1b	1	48.5	49.0	35.3	64.7	1.83
As(V)S-1c	3	14.2	43.0	42.6	57.4	1.35
As(V)S-1d	3	11.5	35.0	41.7	58.3	1.40
As-impreg. silicate-1	1	7.6	8.0	14.3	85.7	7.00

[a] Conditions: catalyst 0.12 g, 1 g phenol, solvent, water 10 g, temp. 80°C, reaction time 12 h.
[b] H_2O_2 utilized in the formation of hydroquinone (HQ), and catechol (CAT).

Table 3
Oxidative dehydrogenation of 2-butanol and benzyl alcohol over As(V)S-1b sample using air. O_2/alcohol = 1 (mole/mole), WHSV (alcohol) = 3.5 h^{-1}

Temp. (°C)	2-butanol (wt%)			Benzyl alcohol (wt%)			
	conv.	2-butanone	others [a]	conv.	ald.	acid	others [b]
350	15.0	90.0	10.0	22.8	87.0	4.0	9.0
350 [c]	5.2	5.0	95.0	nd	–	–	–
400	35.2	78.2	21.8	45.7	83.4	5.4	12.2
400 [c]	8.6	9.5	90.5	nd	–	–	–
450	55.3	65.4	34.7	74.3	80.2	6.6	13.2

[a] Mainly butenes and some dimerized etheric products.
[b] Mainly cleaved products like benzene and HCHO.
[c] Reactions were carried out in the flow of nitrogen, nd = not determined.

Table 3 exhibits the results of vapor phase oxidative dehydrogenation of 2-butanol and benzyl alcohol in the presence of air, carried out in a fixed bed reactor having catalyst size 20–25 mesh. As expected, the conversion increased and selectivity for oxidation products decreased with the increase in reaction temperature suggesting redox nature of the catalyst. However, when 2-butanol was reacted over the same catalyst in the presence of nitrogen, instead of oxygen/air, under otherwise similar reaction conditions, little conversion was observed with almost 90% selectivity towards butenes among products (table 3). These results further suggest that the catalyst (As(V)-silicate-1) does not contain any appreciable basic nature, indicating that As(V) is not present in regular corner sharing T_d environment, instead As(V) may be present as shown in species I.

4. Conclusions

It can be concluded that the MFI type arseno-silicates can be synthesized at as low as 70–90°C in just 8–72 h (both under static and agitating conditions). The crystallization of the As-free pure silica polymorph (silicalite-1) requires higher temperature and more time under otherwise similar conditions, except in the presence of an As source. This is a new phenomenon observed in the synthesis of high silica molecular sieves because the synthesis of other high silica metallo-silicates requires more time than that required for pure silica polymorph. Further, with the increase in the concentration of As(V) in the gel, the crystallization time decreases, a reverse phenomenon compared to other metallo-silicates, where the rate of crystallization increases with increase in silicon/metal molar ratio. Similar results are also observed in the case of other arseno-silicate analogues of MEL, MTW and ZSM-48 topologies [12]. The As(V)S-1 samples are active catalysts in oxidation reactions such as hydroxylation of phenol with dilute H_2O_2, and vapor phase oxidation of 2-butanol to 2-butanone in air, respectively.

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