

Novel mesoporous silicotinphosphate molecular sieve with high anion exchange capacity

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Abstract

New mesoporous silicotinphosphate materials with different Si:Sn:P mole ratios have been synthesized under hydrothermal condition using the self-assembly of cationic surfactant under mild acid pHs and characterized by elemental analysis, XRD, TEM, SEM-EDS, N₂ sorption, FT IR, and UV–vis diffuse reflectance measurements and ion-exchange studies. XRD and TEM results suggested a wormhole-like disordered framework in this material. N₂ adsorption studies revealed that the pore diameters of different samples were 1.7–2.2 nm. FT IR and UV–vis spectroscopic studies suggested the presence of Sn–O–P, Sn–O–Si bonds and tetrahedral coordination of Sn(IV) in these novel mesoporous materials. These novel silicotinphosphate materials showed good anion-exchange capacities (2.56–0.27 mmol g⁻¹, which correspond well with their respective Si:Sn:P mole ratios in the solid products) and catalytic activity in the liquid phase epoxidation of styrene using dilute H₂O₂ as oxidant.
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1. Introduction

Mesoporous silicate and phosphate based molecular sieves [1–4] have received considerable attention over the last decade because of their potential applications in catalysis, adsorption, separations, etc. These materials are also useful for the synthesis of ultrafine nanorod arrays [5] or ordered mesoporous carbons [6] needed for device fabrication. Mesoporous materials containing different hetero-elements found many practical utilities because of the physical and chemical nature of the individual element associated with the framework. The incorporation of Sn(IV) in the tetrahedral silica frameworks of these materials were expected to enhance surface acidity as Sn(IV) salts are well-known strong Lewis acid [7]. Apart from that, tetrahedral Sn present in the framework can act as good oxidation catalyst [8] in the presence of dilute H₂O₂ oxidant. Thus, incorporation of Sn(IV) in the silica network can give an efficient oxidation catalyst in liquid phase partial oxidation reactions. Tin-containing microporous metallosilicates [8,9] have been

reported and utilized in the liquid-phase partial oxidation reactions. Very recently, Sn-Beta has been successfully utilized as a heterogeneous chemo-selective catalyst for the Baeyer–Villiger oxidation reaction with a very high selectivity for the lactone [10]. However, there is a maximum loading limit of Sn(IV) in the tetrahedral silica network, beyond which agglomerated SnO₂ phase start growing.

On the other hand, mesoporous tin phosphate materials reported very recently [11,12] also have many potential utilities. However, due to a very high charge structure, these materials have relatively poor chemical and thermal stability. This could be overcome through the incorporation of Si in tin phosphate based materials similar to the incorporation of Si in AlPO₄ (SAPO based molecular sieves) [13]. Thus, a mesoporous material with Si, P and Sn as an integral part of the oxide framework is highly desirable. These mesoporous materials with diverse framework structures [4–6,14–18] are useful for specific applications. Moreover, anion exchangeable mesoporous frameworks are rare [4,19]. Here, we show that the silicotinphosphate materials with mesostructure could be synthesized with different Si:Sn:P mole ratios in the presence of cationic surfactant under hydrothermal conditions. In this case as high as almost stoichiometric ratio of the constituent elements could be present in

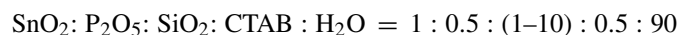
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the framework retaining the same charged structure. This material showed excellent ion-exchange capacity, which could be very effective in removal of arsenic from polluted ground water and good catalytic activity and selectivity in the epoxidation of styrene.

2. Experimental

$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Loba Chemie) was used as Sn source in this study. Tetraethyl orthosilicate (TEOS, Aldrich) and phosphoric acid (85% aqueous, E-Merck) were used as silica and phosphorous precursors, respectively. Cationic surfactant, cetyltrimethylammonium bromide (CTAB, Loba Chemie) was used for structure direction under mild acidic synthesis conditions. In a typical synthesis, initially TEOS was first allowed to mix with an aqueous solution of CTAB and the mixture was stirred for 15 min. Then the required amount of SnCl_4 in water was added onto the solution. TEOS was then allowed to hydrolyze at mildly acidic pH slowly. Then the desired amount of H_3PO_4 was taken in water and added onto this hydrolyzed silica gel. Final pHs of the syntheses gels were between 4.0 and 5.0. The final mixtures were vigorously stirred for another 1 h and then autoclaved at 353 K for 3 days. The molar ratio of various constituents of the hydrothermal gels were



Four silicotinphosphate samples with Sn:P:Si input mole ratios 1:1:1, 1:1:3, 1:1:5 and 1:1:10 have been synthesized and these samples have been designated as 1, 2, 3 and 4, respectively. After the hydrothermal treatment the solid products were filtered, washed with water and dried in air. Surfactants were removed from the as-synthesized materials by acid extraction (acetic acid in dry ethanol) at room temperature for 4 h under stirring. The as-synthesized as well as template-free samples were identified by low angle powder XRD by using a Seifert XRD 3000P diffractometer on which the small and wide-angle goniometers are mounted. The X-ray source was Cu $\text{K}\alpha$ radiation ($\lambda = 0.15406$ nm) with a voltage and current of 40 kV and 20 mA, respectively. For the transmission electron microscopy measurement a JEOL JEM 2010 microscope operated at an accelerated voltage 200 kV was used. N_2 adsorption measurements were carried out using a Quantachrome Autosorb 1-C instrument at 77 K. Prior to N_2 adsorption, samples were degassed for 2 h at 323 K. For the Fourier-transform infrared (FT IR) measurement a Nicolet Magna IR 750 series II spectrophotometer was used. JEOL JEM 6700F field emission scanning electron microscope with an EDS attachment was used for the determination of morphology and surface chemical composition.

The liquid phase reactions were performed in a magnetically stirred round-bottomed flask fitted with a condenser and placed in a temperature controlled oil bath. Typically, 0.01 mol of the substrate was dissolved in 10.0 ml acetonitrile (solvent), and to this was added the required amount of catalyst (20 wt.% with respect to the substrate) and then the mixture was preheated to 353 K. The reaction was started immediately after the peroxide (H_2O_2) was added to the reaction mixture. The substrate to H_2O_2

Table 1

Physico-chemical properties of mesoporous silicotinphosphate samples

Sample number	Si:Sn:P mole ratio		BET surface area ($\text{m}^2 \text{g}^{-1}$)	Anion exchange capacity (mmol g^{-1})
	Gel	Solid		
1	1:1:1	1:0.87:0.83	517	2.56
2	3:1:1	5.8:1.0:0.94	668	1.15
3	5:1:1	11.2:1.0:0.95	726	0.68
4	10:1:1	26.5:1.0:0.90	784	0.27

mole ratio was kept at 1.0 and 2.0 for different set of reactions. Aliquots of the reaction mixtures were taken at regular intervals and after cooling the filtrates the progress of the reactions was monitored by an Agilent 4890D gas chromatograph (FID detector) fitted with a capillary column; 0.5 ml *n*-heptane was introduced to each of the reaction mixtures as internal standard before analysis.

For the ion-exchange measurements 1 g of template-free sample was taken in 100 ml 1 M KCl solution and this solution was stirred for 4 h. This was followed by filtration. Chloride content in the initial KCl solution and final filtrate were determined through titration by using a 1 M AgNO_3 solution and potassium chromate indicator. By subtracting the Cl^- concentration in the filtrate from the initial solution, exchanged Cl^- concentration and thus anion exchange capacity was determined.

3. Results and discussion

Physico-chemical properties of these silicotinphosphate samples are given in Table 1. Chemical analysis of these silicotinphosphate samples after the acid-solvent extraction revealed the absence of any organic SDA. Si/Sn mole ratios for samples 1, 2, 3 and 4 were 1.15, 5.82, 11.2 and 26.5. XRD patterns of the silicotinphosphate samples 1, 2, 3 and 4 are shown in Fig. 1(a–d). As seen from Fig. 1, only one low-angle peak for d_{100} plane

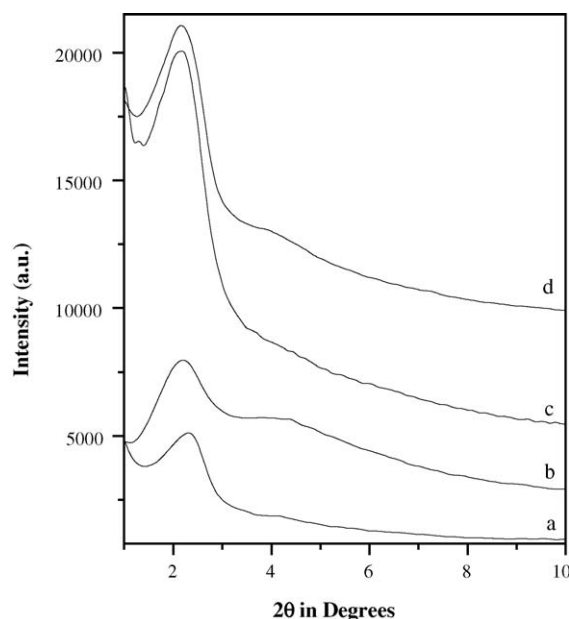


Fig. 1. XRD patterns of silicotinphosphate samples 4 (a), 2 (b), 3 (c) and 1 (d).

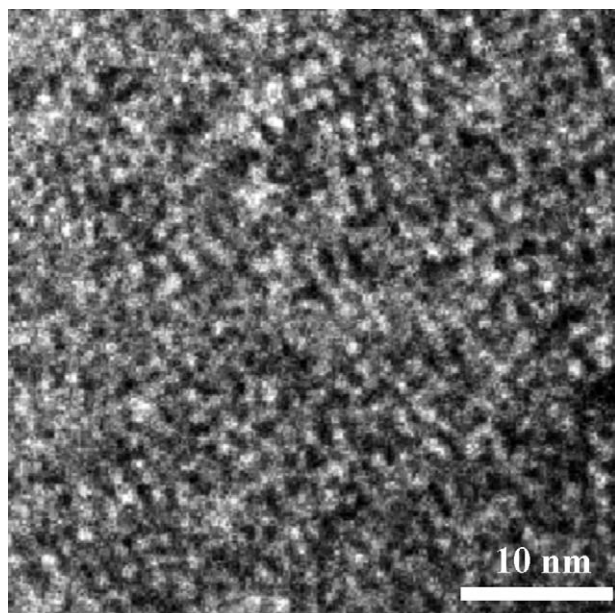


Fig. 2. TEM image of sample 2.

corresponding to the disordered mesophase [20] were observed in all the samples. No distinctive higher order peaks were observed in either of the samples. As seen from Fig. 1 with the increase in silicon loading in the gel, broadening of the XRD peak, indicative of more disordered porous structure was observed. The peak positions remained almost unchanged after removal of the surfactant. No diffraction line corresponding to tin oxide crystallites were observed in either of the samples synthesized by this method. This result suggested that no occluded tin oxide species were formed. TEM image of these mesoporous samples (Fig. 2) showed the existence of wormhole-like structures. These results suggested that the frameworks for these novel materials have disordered mesophase.

In Fig. 3, N_2 adsorption/desorption isotherms for silicotinphosphate (samples 1 and 2) are shown. Pore size distributions are shown in the inset. Isotherms, as shown in Fig. 3 were type IV [21] in nature. Pore size distributions were very narrow. Average pore diameter for this silicotinphosphate sample 2, calculated by employing the BJH model, was 2.13 nm. The BET surface areas for these silicotinphosphate samples were medium to high (Table 1), considering moderately high concentration of tin.

In Fig. 4 UV–vis diffuse reflectance spectra of mesoporous silicotinphosphate samples (b–e, for samples 4, 3, 2 and 1, respectively) are shown. The spectrum for bulk SnO_2 is given in Fig. 4(a) for comparison. The UV–vis spectra of the silicotinphosphate materials showed a strong absorption band in the 200–320 nm wavelength. A similar absorption band associated with ligand to metal charge transfer for the isolated tetrahedral coordination of Sn^{4+} has been observed for microporous tinsilicate [8] and mesoporous tinphosphate [11]. Bulk SnO_2 showed a broad adsorption band in the range of 220–400 nm and mild absorption maximums at 470 and 610 nm (Fig. 4a). However, for sample 1 (Fig. 4e) with almost equal molar ratio of Si, Sn and P, a strong absorption at 310 nm and weak absorption at 241 and 213 nm were observed. The additional band at 310 nm

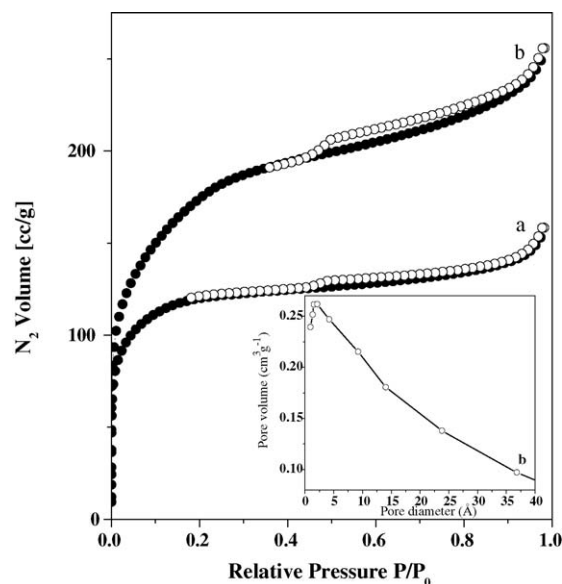


Fig. 3. N_2 adsorption/desorption isotherms of samples 2 (a) and 1 (b). Adsorption points are marked with filled circles and that for desorption by empty circles. Pore size distribution of sample 1 has been shown in the inset.

could be attributed due to $Sn(IV)$ interacting with the counter anion in the silicotinphosphate framework. This result suggested that the tetrahedral coordination of $Sn(IV)$ dominates in these mesoporous silicotinphosphate samples.

The FT IR spectra of the surfactant-free silicotinphosphate samples are shown in Fig. 5. A broad band in the hydroxyl region between 3700 and 3000 cm^{-1} with maximums at 3450 and 3212 cm^{-1} were observed. This broad band at 3450 cm^{-1} could be assigned due to the framework $Si-O-H$, $P-O-H$, and $Sn-O-H$ as well as $Si(OH)Sn$ groups in interaction with the defect sites and adsorbed water molecules. Framework vibra-

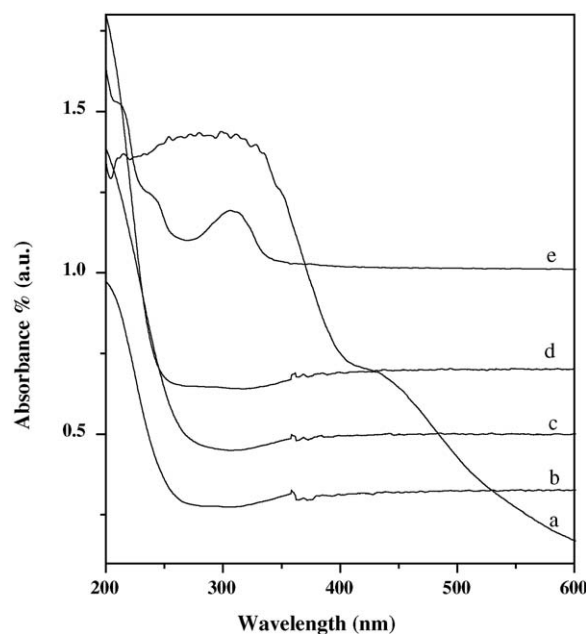


Fig. 4. UV–vis diffuse reflectance spectra of SnO_2 (a) samples 4 (b), 3 (c), 2 (d) and 1 (e).

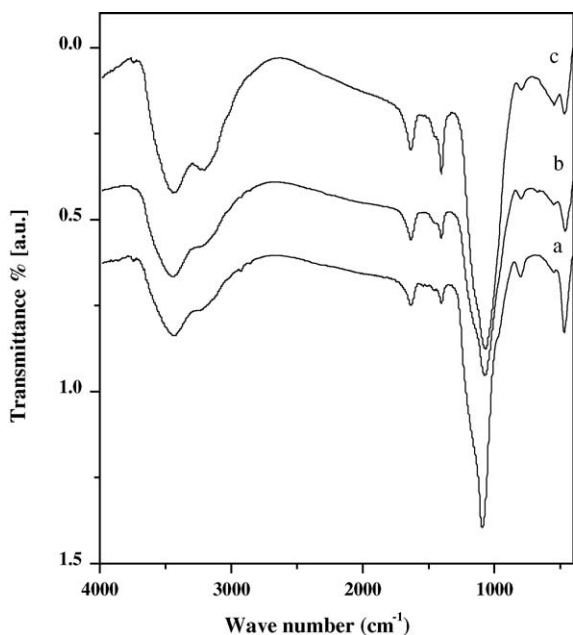


Fig. 5. FT IR spectra of samples 2 (a), 3 (b) and 1 (c).

tions, which appear in the region of $860\text{--}1400\text{ cm}^{-1}$, became much narrower in the region of $900\text{--}1360\text{ cm}^{-1}$ after surfactant removal. In Fig. 6 SEM image of a representative (sample 1) mesoporous silicotinphosphate is shown. Very tiny spherical nanoparticles of $10\text{--}12\text{ nm}$ dimension were found to form large aggregates. Chemical analysis (using EDS, Fig. 7) data at different point of the image suggested almost uniform distribution of O, Si, P and Sn for all the samples. KCl exchanged sample 1 showed considerable amount of Cl^- in the solid (Fig. 7).

Supramolecular assembly of cationic surfactant micelles in aqueous (acidic/basic) solutions are usually employed for the synthesis of silica based mesoporous materials. pH in such synthesis processes play crucial role in the formation of par-

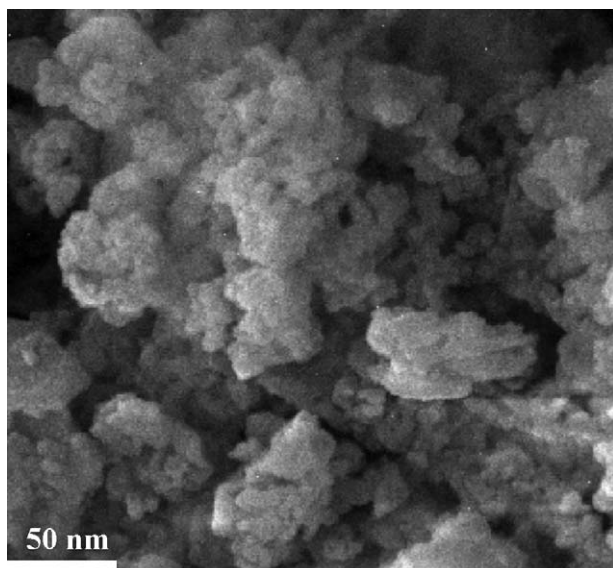


Fig. 6. SEM image of sample 1.

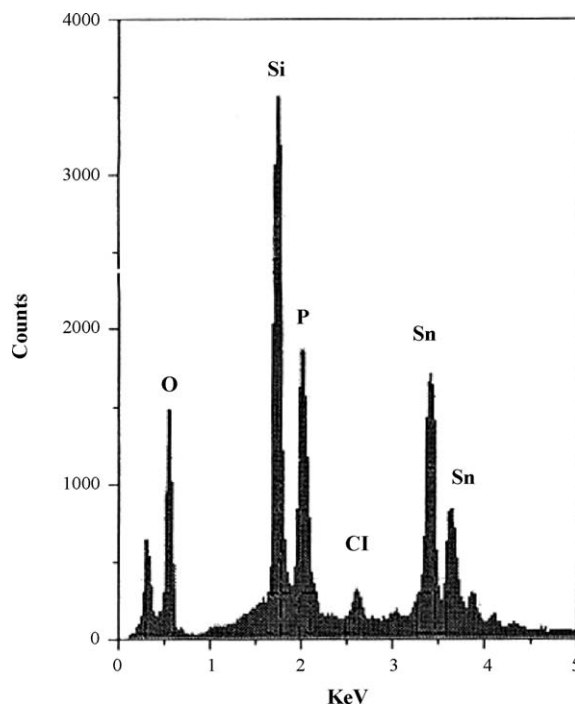


Fig. 7. EDS pattern of Cl^- exchanged sample 1.

ticular mesophase. In the present case, silicon alkoxide was first hydrolyzed by strongly acidic stannic chloride solution in water. This was followed by the condensation of silica with Sn^{4+} and PO_4^{3-} as the pH dropped with the addition of orthophosphoric acid. The final pH of the hydrothermal gels were kept in the range of pH $4.0\text{--}5.0$, which could help the condensation of tin phosphate with the silicate nuclei rather than that between individual silicate and SnPO_4 moieties. The self-assembly of the surfactant-silicate mesostructure is largely dependent on the strong ionic interaction between surfactant micelles and inorganic metallo-silicate species. Here possibly the interaction of the cationic surfactant with the defect Si-OH and P-OH sites or the counter anion (Cl^-) mediation took place, leading to mesoporous silicotinphosphate.

3.1. Ion-exchange studies

Ion-exchange capacity of the solid often uses the semi-quantitative method for the determination of the framework structure of the material. In Table 1 Cl^- exchange capacity for different samples are given. With the decrease in Sn and P contents in the samples similar decrease in anion exchange capacity were observed and the elemental analysis data (Table 1) suggested the incorporation of almost one equivalent of Cl^- for each tinphosphate moiety in the framework. This anion exchange capacity could be observed for the metallo (IV) phosphates due to the presence of framework positive charge as observed for mesoporous titanium [6], tin [11] and niobiumphosphates [22] etc.

High anion exchange capacity observed in these mesoporous silicotinphosphates guided us to explore the possibility of the removal of arsenic from polluted ground water. Most common

Table 2
Arsenic removal efficiency of mesoporous silicotinphosphate^a

Entry	Solution type	Arsenic content (mg/l)		Arsenic removal efficiency (%)
		Before	After	
1	~200 ppb As(III)	0.206	0.113	45.2
2	~200 ppb As(III) + 0.2 g H ₂ O ₂	0.206	0.023	89.0

^a 100 g of each of the solution was treated with 0.5 g pre-treated mesoporous silicotinphosphate sample 1 for 4 h at 298 K in a closed reaction vessel under O₂ atmosphere. Double distilled water with arsenic content below AAS detectable limit was used for the preparation of the standard As(III)/As(V) solutions.

Table 3
Epoxidation of styrene catalysed by silicotinphosphate materials^a

Sample number	Reaction time (h)	% Conv. of styrene	H ₂ O ₂ sel. (%)	Product selectivity (%)		TON ^b (h ⁻¹)
				Styrene-oxide	Diols	
1	36	88.5	100	85.8	14.2	11.65
2	30	57.0	100	88.9	11.1	7.50
3	36	43.4	96	82.2	17.8	5.71
4	40	48.4	68	92.0	8.0	6.38
– ^c	30	0.8	1.2	100.0	–	–

^a Solvent acetonitrile; catalyst = 20 wt.% with respect to the substrate, substrate: H₂O₂ = 1:1 unless otherwise mentioned.

^b Turn over number, moles of styrene converted per mole of Sn per hour.

^c Blank reaction in absence of catalyst.

valence state of arsenic observed in water is arsenate, As(V), which occurs mostly in aerobic surface waters and arsenite, As(III), found in anaerobic ground water. In the pH range of 4–8, the predominant As(V) species are H₂AsO₄⁻ and HAsO₄²⁻, which are negatively charged, and thus easy to get exchanged by an anion exchanger, whereas As(III) remained mostly non-ionized H₃AsO₃. As(III) can be easily oxidized by mild oxidants like H₂O₂. Cationic sites present in the frameworks of the mesoporous functionalized silica materials with surface amines [23] and layered double hydroxides [24] have been used as efficient exchanger for the removal of pollutant anions. In Table 2 arsenic removal efficiency of mesoporous silicotinphosphate sample 1 from a ~200 ppb arsenic containing NaAsO₂ solution with or without very small amount of dilute H₂O₂ have been given. As content has been drastically reduced to a level acceptable as drinking water. A detailed exchange study on these novel materials is underway and will be published soon.

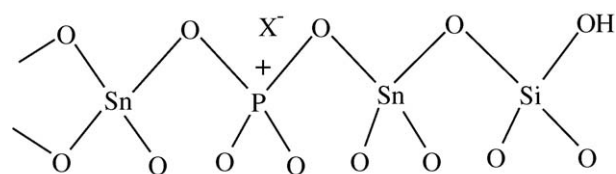
3.2. Liquid phase catalysis

Tin containing mesoporous silicotinphosphate materials were used as catalysts for the epoxidation of styrene by using dilute aqueous H₂O₂ as oxidant. Metallosilicates are well-known catalysts for the epoxidation of olefins using dilute aqueous H₂O₂ as oxidant [25]. Oxidation of styrene has been achieved under different critical reaction conditions [26]. The conversion and the selectivity of different oxidized products over mesoporous silicotinphosphate samples are listed in Table 3. These mesoporous materials exhibited a good catalytic performance along with very high selectivity towards epoxide product. Like mesoporous Cr-MCM-41 [27] and Co-MCM-41 [28] molecular sieves here also we have checked for any hypothetically leached Sn species under similar reaction conditions. We found no activity in the

liquid phase alone after filtering out the catalyst from the reaction media. It is evident that no Sn species leached out of the catalyst and the reaction was stopped after catalyst removal. Thus it can be concluded that the activity of the catalyst was due to the Sn active centers as observed previously over other Sn-containing molecular sieves [8–11]. A blank reaction in the absence of catalyst showed almost no conversion (Table 3, entry 5) indicating that the oxidation of styrene is purely catalytic in nature.

We propose a model for the Si, Sn, P and O connectivity in the framework of the silicotinphosphate mesoporous materials based on the above results, as shown in Fig. 8. Si, Sn and P have regular alternating tetrahedral arrangements. Whereas Si and Sn atoms are neutral in nature, one positive charge resides on P atoms, which could be balanced by the counter anions. Self-assembly of the cationic surfactant directs the formation of this novel framework structure. Hence, the defect P–OH and Si–OH sites may be responsible for some cation exchange sites in these samples also. This model explains the ion exchange capacities of these materials.

Mesoporous tinphosphates [11,12] with tetrahedral Sn(IV) have been hydrothermally synthesized using cationic alkyltrimethylammonium bromide (alkyl, C₈–C₁₈) as surfactant via lamellar mesophases of tinphosphate materials.



Where X⁻ = OH⁻, Cl⁻ etc.

Fig. 8. Proposed framework structure of the mesoporous silicotinphosphate.

During secondary treatment with H_3PO_4 , possibly the inherent anion exchangeable sites of the tinphosphate framework get exchanged with strongly bound additional PO_4^{3-} ions, which may in turn be responsible for its high thermal stability and acid catalytic properties. But here the mesoporous silicotinphosphate has been synthesized hydrothermally in one step, which may help the formation of more open structure with anion exchangeable sites. Spectroscopic data suggested the tetrahedral coordination of Sn(IV) in this material. This additional anion exchange site corresponding to each tinphosphate moiety in the silicotinphosphate framework is responsible for high anion exchange capacity of this novel material.

4. Conclusions

Mesoporous silicotinphosphate materials have been synthesized using cationic surfactant as structure directing agent under mildly hydrothermal condition and at weakly acidic pH. With the decrease in silicon concentration more disordered mesophase with XRD peak broadening was observed. N_2 adsorption measurements indicated medium to high BET specific surface area, uniform mesopore opening and high pore volume in these samples. UV–vis diffuse reflectance and FT IR spectra suggested the Si–O–Sn–O–P network in this material. These silicotinphosphate samples showed considerable anion exchange capacity for the removal of arsenic (H_2AsO_4^- and HAsO_4^{2-} ions) from polluted ground water and catalytic activity in the liquid phase oxidation of styrene to styrene-oxide using dilute H_2O_2 as oxidant.

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