Synthesis and catalytic properties of large-pore Sn-β and Al-free Sn-β molecular sieves

N. K. Mal and A. V. Ramaswamy*

National Chemical Laboratory, Pune-411 008, India

Sn-β and Al-free Sn-β (large pore, 12-membered ring channels) molecular sieves prepared by hydrothermal synthesis and characterised by XRD, FTIR and sorption techniques are distinguished by their acidic and oxidation properties, in the acetylation of 1,3,5-trimethylbenzene (1,3,5-TMB) with acetyl chloride and in the oxidation of *m*-cresol and 1,3,5-TMB with aqueous H_2O_2, respectively.

Following the synthesis of medium-pore (10-membered ring) TS-1[1] and its use in shape-selective oxidation reactions on a commercial scale in the hydroxylation of phenol,[2] many attempts have been made to synthesize large pore (12 MR), three-dimensional Al-free Ti-β, without much success, unless trivalent metal ions of Al^{3+} were present in the lattice.[3–6] Recently, Camblor *et al.*[7] reported the synthesis of Al-free Ti-β using seed crystals, and this material has been used effectively for the epoxidation of alkenes and for oxidation of relatively bulkier organic substrates.[8] We earlier reported the synthesis of medium-pore Sn-sil-1 (MFI structure), which was found to be less active than TS-1 in the hydroxylation of phenol[9] but more active than TS-1 in the oxidation of ethylbenzene[10] under similar conditions. In this report, for the first time, we describe the synthesis of large-pore, Sn-β and Al-free Sn-β molecular sieves, their characterization by XRD, FTIR and sorption techniques and catalytic activity in the hydroxylation of phenol, oxidation of *m*-cresol and 1,3,5-TMB in presence of aqueous H_2O_2 and acetylation of 1,3,5-TMB with acetyl chloride (AcCl).

The hydrothermal synthesis of Sn-β was carried out using gels with the following molar composition: 1.0 SiO_2 : 0.0–0.0125 SnO_2 : 0.0–0.03 Al_2O_3 : 0.52–0.70 TEAOH : 20 H_2O. In a typical preparation, 0.71 g of $SnCl_4 \cdot 5H_2O$ (98%, Loba Chem) in 10 g of H_2O was added to 41.7 g of tetraethylorthosilicate (TEOS) (99.9%, Aldrich). After 15 min, 58.9 g of tetraethylammonium hydroxide (TEAOH) (35 mass% aqueous solution, Aldrich) was added under vigorous stirring for 1 h. To this reaction mixture 0.63 g of $Al_2(SO_4)_3 \cdot 16H_2O$ in 15 g H_2O was added and stirred for another 1 h. 8.7 g of H_2O was then added to the clear solution and stirred for 2 h. The resultant clear solution was charged into a stainless-steel autoclave and heated at 415 K under autogenous pressure and static conditions for 10 days to complete the crystallization. The resultant product was filtered, washed with deionized water, dried at 383 K and calcined at 823 K for 16 h. This sample is referred to as A. One more such Sn-β sample was prepared with different Al and Sn contents (Si/Al = 30.0 in gel and 14.7 in crystalline product and Si/Sn = 200 in gel and 150 in crystalline product). Dealuminated Sn-β (sample B) was prepared by refluxing 4 g of sample A with 60 ml of 5 m HCl for 3 h at 383 K. This treatment was repeated once more after filtration. This sample was filtered and washed thoroughly with distilled water until free of all acid and finally dried and calcined at 723 K for 12 h. Sample C was prepared following a similar procedure that was used for the synthesis of sample A, except that 0.5 g of B was added in place of 0.63 g of $Al_2(SO_4)_3 \cdot 16H_2O$. Two β zeolite samples (without Sn) were also prepared with different SiO_2/Al_2O_3 ratios (30.0 and 250). Al-free β (or silicalite) was prepared by the dealumination of zeolite-β of SiO_2/Al_2O_3 molar ratio of 250.

The XRD profiles of all as-synthesized and calcined samples match well with the BEA topology. No peaks due to SnO_2 or crystalline impurity phases are seen. The crystallinity of as-synthesized β is maximum, and this sample was considered to be the reference sample. Sn-β (A), Al-free Sn-β (C), dealuminated Sn-β (B) and dealuminated β (silicalite) are relatively less crystalline (approximately 96, 87, 67 and 55%, respectively) with respect to the reference sample. The SEM micrographs show that the particle size of all the samples is < 0.3 μm. The framework IR spectra of Sn samples (in Nujol mull) show a peak at *ca.* 957 cm^{-1} (Fig. 1). This band which is intense in the case of Al-free Sn-β (C), is not observed in Sn-free β-zeolites. This band has been assigned to Si–O–M vibrations or Si–O(H) defect groups promoted by framework M from the possible substitution of heteroatom (M) in the Si–O–Si units.[9,10] N_2 adsorption isotherms at 77 K of Sn-β samples are characteristic of microporous materials. The surface areas are typically in the region of 650 $m^2\ g^{-1}$ for all the samples (Table 1). The mesopore (*t*-area) contribution is rather small in the case of Sn-β and Al-free Sn-β samples (35.6 and 57.0 $m^2\ g^{-1}$, respectively) but significant in the dealuminated β samples (120–160 $m^2\ g^{-1}$). The micropore volumes are in the range 0.20–0.25 ml g^{-1} for all samples. The amounts of H_2O, *n*-hexane, cyclohexane and *m*-xylene adsorbed on these samples at 298 K and at p/p_o of 0.5 (gravimetric, Cahn electrobalance) are included in Table 1. The comparable sorption capacity of Sn-containing and Sn-free β samples indicates that the micropore volumes are well maintained and that occluded SnO_2-type species may not be present in the Sn-containing samples.

The results on the catalytic activity of all the β samples are summarised in Table 2. The catalytic activity of the β, Sn-β and

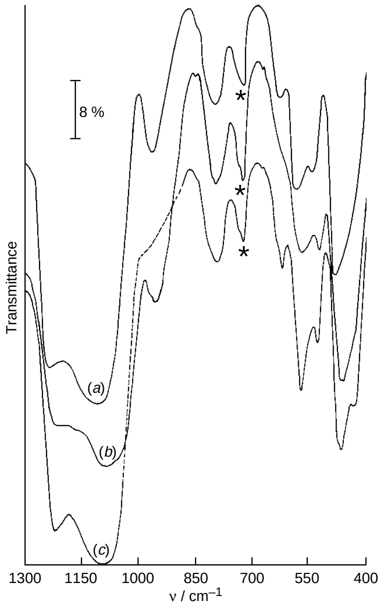

Fig. 1 FTIR spectra of Al-free Sn-β sample (*a*), Sn-β sample with Si/Al = 28.5 and Si/Sn = 78.8 (*b*) and β sample with Si/Al = 50.3 (*c*). The absorption at 957 cm^{-1} is similar to that observed for Ti-, V- and Sn-MFI and -MEL structures. * Nujol peak.

Table 1 Physicochemical characteristics of Sn-β zeolites[a]

Sample	In gel, molar ratio		Products, molar ratio[a]		Sorption capacity[b] (mass%)				Surface area[c]/m^2 g^{-1}	Micropore volume/ml g^{-1}
	Si/Sn	Si/Al	Si/Sn	Si/Al	H_2O	*n*-hexane	cyclohexane	*m*-xylene		
Sn-β (A)	100	100	78.8	28.5	26.7	19.3	21.2	25.0	670	0.25
deAl-Sn-β (B)	—	—	85.4	> 3000	23.3	18.6	20.4	23.9	665	0.22
Al-free Sn-β (C)	100	—	54.5	> 4000	25.6	19.4	21.3	25.4	677	0.25
β	—	125	∞	50.3	20.5	18.8	20.7	24.2	652	0.23
deAl-β (silicalite)	—	—	—	> 3000	18.4	18.2	19.7	22.3	645	0.20

[a] Chemical analysis using EDX and ICP. [b] Gravimetric adsorption at $p/p_o = 0.5$ and at 298 K (Cahn electrobalance). [c] N_2 adsorption isotherms (Coulter 100 CX analyser) at 77 K.

Table 2 Reactions over Sn-containing β zeolites[a]

Sample	Products, molar ratio		Phenol hydroxylation[b]		Oxidation of *m*-cresol[c]		Oxidation of 1,3,5-TMB[d]			Acetylation of 1,3,5-TMB[e]	
	Si/Sn	Si/Al	TON	H_2O_2 efficiency	TON	H_2O_2 efficiency	TON	H_2O_2 efficiency	Selectivity[f]	AcCl conv.[g]	Selectivity[h]
Sn-β (A)	78.8	28.5	30.3	33.0	6.6	20.3	1.0	4.2	50	32.5	96.5
deAl-Sn-β (B)	85.4	> 4000	83.6	44.7	32.3	52.3	7.7	18.9	80	—	—
Al-free Sn-β (C)	54.5	> 3000	80.1	65.0	30.6	75.4	6.6	24.5	77	6.4	99.1
β	∞	50.3	8.8	8.1	1.3	4.6	0.0	0.0	0.0	34.8	83.6
Sn-β	150	14.7	—	—	—	—	—	—	—	99.9	94.6
β	∞	13.9	—	—	—	—	—	—	—	99.9	82.0

[a] Catalyst/substrate = 10, 20, 20 mass% in the case of phenol, *m*-cresol and 1,3,5-TMB, respectively; substrate/H_2O_2 (mole) = 3.0; solvent/substrate (mole) = 20; reaction time = 15 h; TON is defined as the mole of substrate converted per mole of metal ion (Al + Sn). [b] Batch reactor; $T = 348$ K; solvent = H_2O, H_2O_2 efficiency = mol% H_2O_2 consumed in the formation of parabenzoquinone, catechol and hydroquinone. [c] Parr autoclave; $T = 373$ K; solvent = H_2O : acetonitrile (2 : 1), H_2O_2 efficiency = mol% H_2O_2 consumed in the formation of 2,5-dihydroxytoluene, 3,4-dihydroxytoluene, 3-hydroxybenzyl alcohol and 3-hydroxybenzaldehyde. [d] Batch reactor; $T = 348$ K; solvent = acetonitrile, H_2O_2 efficiency = mol% H_2O_2 consumed in the formation of 3,5-dimethylbenzyl alcohol, 3,5-dimethylbenzaldehyde and 2-hydroxy-1,3,5-TMB. [e] Down-flow, fixed-bed reactor; $T = 428$ K; 1,3,5-TMB/acetyl chloride (AcCl) (mol) = 3.0, WHSV = 1.0 h^{-1}, analysis after 1 h run. [f] Product selectivity (mass%) for 3,5-dimethylbenzaldehyde. [g] Conversion (mass%) of acetyl chloride (AcCl). [h] Product selectivity for 2,4,6-trimethylacetophenone.

Al-free Sn-β samples can be rationalised in terms of activity due to acidic properties (depending on the Si/Al ratio) and oxidation properties (isolated Sn^{4+} sites) or a combination of the two. All the Sn-containing samples are active in the hydroxylation of phenol, and oxidation of *m*-cresol and 1,3,5-TMB with aqueous H_2O_2 to different degrees. Both deAl-Sn-β (B) and Al-free Sn-β (C) samples show consistantly higher H_2O_2 efficiency in all the three test reactions, indicating the absence of acid sites (Si/Al > 3000). Al-free β (silicalite) shows negligible activity in the oxidation of *m*-cresol and 1,3,5-TMB (no active Sn^{4+} ions) and in the acetylation of 1,3,5-TMB (no acidity). In the hydroxylation of phenol and oxidation of *m*-cresol and 1,3,5-TMB, the H_2O_2 efficiency over deAl-Sn-β (B) was lower than over Al-free Sn-β (C), while the TON is in the same order. The H_2O_2 efficiency in hydroxylation of phenol over Sn-containing β samples was less than that obtained with Sn-sil-1 (MFI structure).[9] This may be due to the more selective nature of the medium-pore Sn-sil-1 than the large pore Sn-containing β samples for relatively small molecules like phenol. In the oxidation of *m*-cresol, 75.4 mol% H_2O_2 efficiency could be achieved over Al-free Sn-β and 2-methylhydroquinone was detected as the major product. In the oxidation of *m*-cresol, both deAl-Sn-β (B) and Al-free Sn-β (C) show better H_2O_2 efficiency (18.9 and 24.5%, respectively) and TON (7.7 and 6.6, respectively) than Sn-β (A) (H_2O_2 efficiency = 4.2% and TON = 1.0). Sn-β (A) is not a good catalyst for the oxidation reaction. 3,5-Dimethylbenzaldehyde was detected as the major product in the oxidation of 1,3,5-TMB.

The β and Sn-β zeolites are active in the acetylation of 1,3,5-TMB with acetyl chloride. Under the conditions of the reaction, the conversion of acetyl chloride is related to the acidity (Si/Al ratio) of the sample. While both Sn-β (Si/Sn = 150 and Si/Al = 14.7) and β (Si/Al = 13.9) give a very high conversion (99.9%) of acetyl chloride, the selectivity for 2,4,5-trimethylacetophenone is higher on Sn-β (94.6%) than on β zeolite (82.0 mass%). The reason for the enhancement of selectivity over Sn-containing β zeolite is not clear at the moment. When the acetylation of 1,3,5-TMB was carried out in the absence of any catalyst (only porcelain beads were loaded in the reactor), the conversion of acetyl chloride was only 5.2%, which is slightly less than over Al-free Sn-β (C) sample (6.4%). This indicates that very weak acidity is associated with Sn^{4+} ions in the zeolite structure.

In conclusion, a large-pore zeolite (BEA) with Sn in the framework has been synthesized for the first time, which is able to catalyse oxidation of bulkier organic substrates with aqueous H_2O_2 in the absence of acidity (Al-free state) and acetylation with acetyl chloride when acidic (low Si/Al ratio), with some selectivity advantages due to the presence of Sn^{4+} ions.

Nawal Kishore is thankful to CSIR, New Delhi for a senior research fellowship.

References

1 M. Taramasso, G. Perego and B. Notari, *US Pat.*, 4,410,501, 1983.
2 B. Notari, *Stud. Surf. Sci. Catal.*, 1987, **47**, 413.
3 R. B. Borade and A. Clearfield, *Microporous Mater.*, 1996, **5**, 289.
4 M. A. Camblor, M. Constantini, A. Corma, P. Esteve, L. Gilbert, A. Martinez and S. Valencia, *Appl. Catal. A: General*, 1995, **133**, L185.
5 M. A. Camblor, A. Corma, A. Martinez and J. Pèrez-Pariente, *Zeolites*, 1993, **13**, 82.
6 M. A. Camblor, A. Corma, A. Martinez and J. Pèrez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1992, 589.
7 M. A. Camblor, M. Costantini, A. Corma, L. Gilbert, P. Esteve, A. Martinez and S. Valencia, *Chem. Commun.*, 1996, 1339.
8 A. Corma, M. A. Camblor, P. Esteve, A. Martinez and J. Pèrez-Pariente, *J. Catal.*, 1994, **145**, 151.
9 N. K. Mal, V. Ramaswamy, S. Ganapathy and A. V. Ramaswamy, *J. Chem. Soc., Chem. Commun.*, 1994, 1933.
10 N. K. Mal and A. V. Ramaswamy, *Appl. Catal. A: General*, 1996, **143**, 75.

Received, 15th October 1996; Com. 6/07038H