

Evidence for the simultaneous incorporation of Al and Ti in MFI structure (Al-TS-1)

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Simultaneous incorporation of Al and Ti in the MFI-type framework is demonstrated by XRD, i.r. ^{29}Si , and ^{27}Al MAS n.m.r. techniques. The evidence for the presence of both Al and Ti in the silica matrix has been obtained by ^{29}Si MAS n.m.r. as well as by framework i.r. (960 cm^{-1}), XRD (unit cell expansion), ion-exchange capacity ($\text{K}^+/\text{AlO}_2^- = 0.96$), and catalytic properties for acid and oxidation functions in aluminotitanium silicate (Al-TS-1) molecular sieves.

Keywords: Al-TS-1; zeolite synthesis; zeolite characterization; ^{29}Si MAS n.m.r.

INTRODUCTION

The discovery of crystalline titanium silicalite with an MFI structure, TS-1,¹⁻³ has extended the use of molecular sieves in oxidation reactions.³⁻⁶ The incorporation of trivalent metal ions in TS-1 (Al-TS-1^{7,8}) enables them to have both oxidation and acidic properties. This may further enlarge the use of these aluminotitanium silicates as a catalyst. We now report our preliminary findings on the synthesis and characterization of a crystalline, microporous aluminotitanium silicate with MFI structure (Al-TS-1). This material is catalytically active in both acid-catalyzed and oxidation reactions. The presence of both Al and Ti in the MFI framework positions in Al-TS-1 is confirmed by ^{29}Si and ^{27}Al MAS n.m.r. spectroscopy for the first time. The sample was further characterized by XRD, framework i.r., and catalytic reactions (isomerization/disproportionation of *m*-xylene and oxidation of benzene to phenol with H_2O_2).

EXPERIMENTAL

Synthesis

Al-TS-1 molecular sieve was synthesized as follows: 80 g tetrapropylammonium hydroxide (20 wt% aqueous solution, Aldrich) was added under stirring to a mixture containing 45.5 g tetraethyl orthosilicate (98%, Aldrich) and 10 g isopropyl alcohol (IPA). This mixture was stirred for 30 min before adding to it a solution of 2.25 g titanium butoxide in 10 g dry IPA.

This clear mixture was stirred for an additional 30 mins. Then, a solution of 1.02 g aluminum isopropoxide in 10 g IPA was added to the above mixture. Finally, 75 g double-distilled water was added slowly and the clear solution was stirred for 3 h at 340 K in order to remove the alcohol. Crystallization was carried out at 433 ± 1 K under static conditions for 3 d.

For comparison, other molecular sieves (TS-1, silicalite-1, and ZSM-5) were synthesized and characterized by methods published earlier.^{4,9-11} The catalytic reactions were carried out over the H-form of the zeolites. The latter were obtained by calcination in air at 773 K (to remove the organics), ammonium exchange, and recalcination in air at 723 K.

Characterization

The crystalline-phase identification was carried out by XRD (Rigaku, MAX-3D). The chemical analysis was performed by wet chemical methods and using atomic absorption (Hitachi Z-800) and ICP (Jobin Yuon-JY VHR) spectrometers. The zeolites were further characterized by i.r. spectroscopy (Perkin-Elmer 221), scanning electron microscopy (Sterioscan Model 150), adsorption, and ion-exchange capacity. The solid-state ^{29}Si and ^{27}Al MAS n.m.r. spectra were recorded at ambient temperature using a Bruker MSL-300 FT-n.m.r. spectrometer. Three thousand FIDs were accumulated before FT to obtain spectra with good S/N ratios. A 5 s delay time was used between each 90° pulse. TMS was used as the external reference for the ^{29}Si signal, while an aqueous solution of AlCl_3 provided the reference peak for ^{27}Al . MAS was kept at 3.5 kHz for all samples. The catalytic runs were carried out in batch^{3,4} (benzene hydroxylation) and vertical down-flow glass reactors (*m*-xylene isomerization). The products were analyzed in a gas chromatograph (Hewlett Packard 5880 A).

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Table 1 Evidence for simultaneous incorporation of Ti and Al in Al-TS-1

Catalyst	Si/Ti	Si/Al	Unit cell volume (Å) ³	Si-O-Ti i.r. band (960 cm ⁻¹)	Ion-exchange capacity ^a	Benzene hydroxylation ^b			
						Benzene conversion (wt%)	H ₂ O ₂ selectivity (%) ^c	Products (mol %)	
								Phenol	<i>p</i> -Benzoquinone
Silicalite-1	—	—	5344	No	Nil	0	—	—	—
TS-1	23	—	5371	Yes	Nil	13	100	75	25
ZSM-5	—	33	5360	No	0.98	3	27	100	—
Al-TS-1	24	45	5380	Yes	0.96	5	40	95	5

^a Molar ratio of K⁺/(AlO₂)⁻^b Reaction conditions: Temp. (K) = 300; benzene/H₂O₂ (mole) = 10; reaction time = 12 h; cat. wt. 1.5 g; 0.0085 mole of H₂O₂/g cat.^c Selectivity to hydroxylation products. The balance was decomposed to H₂O + ½ O₂; H₂O₂ conversion was 100% in all the cases.

RESULTS AND DISCUSSION

The Si/Ti and Si/Al molar ratios in Al-TS-1 were 24 and 45, respectively. Scanning electron microscopic analysis revealed that the average crystal size of the Al-TS-1 ranged between 0.5 and 1.0 μm. The crystals were cuboid in shape. The physicochemical properties of silicalite-1, TS-1, ZSM-5, and Al-TS-1 are presented in Table 1. The unit cell dimensions were calculated from powder XRD patterns for silicalite-1, TS-1, ZSM-5, and Al-TS-1, and the cell volumes were 5344, 5371, 5360, and 5380 (Å)³, respectively. The observed increase in unit cell volume on incorporation of Ti and Al, as expected, is indicative of the presence of both Al and Ti in the MFI framework. Framework i.r. spectra of calcined Al-TS-1 exhibited a band at 960 cm⁻¹, in addition to the bands typical of the pentasil framework. Such a band (at 960 cm⁻¹) characteristic of titanium silicate molecular sieves^{1-4,9-11} had been attributed to an asymmetric stretching mode of a (SiO₄) unit bonded to a Ti⁴⁺ ion (O₃SiOTi). Though the ion-exchange capacities of silicalite and TS-1 were negligible, ZSM-5 and Al-TS-1 had ion-exchange capacities proportional to their aluminum content.

The solid-state ²⁹Si MAS n.m.r. spectroscopic results of calcined silicalite-1, TS-1, Al-TS-1, and ZSM-5 are compared in Figure 1 (curves a-d, respectively). The broad peak around -116 ppm (b,c) has been ascribed^{3,10,11} to Si in distorted tetrahedra containing Si-O-Ti bonds, and we have shown recently that the peak intensity (-116 ppm) and line broadening increases with increasing Ti content in TS-1.¹⁰ The intense ²⁹Si peak around -112 ppm and a small peak around -104 ppm (c,d) are commonly attributed to Si bonded with 0 Al [Si(0 Al)] and 1 Al [Si(1 Al)], respectively,¹² indicating the presence of Al of the tetrahedral zeolite framework. Further, ²⁷Al n.m.r. spectra of Al-TS-1 (not presented) showed only one ²⁷Al signal at 56 ppm (with respect to aq. AlCl₃), indicating the presence of Al in T_d symmetry.

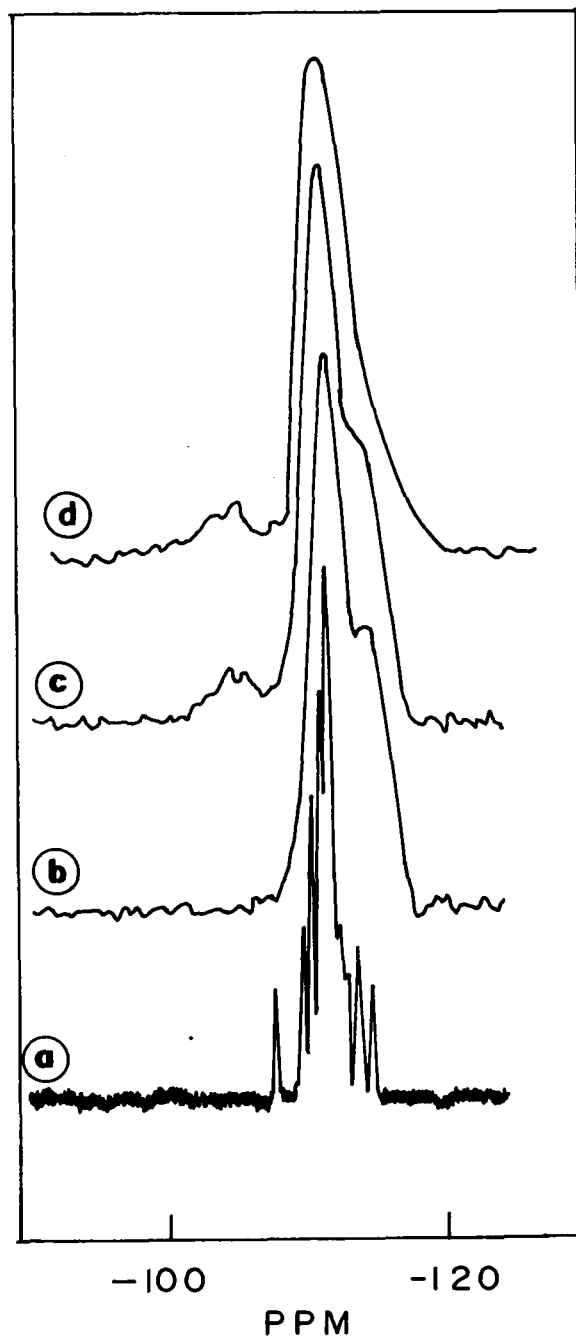


Figure 1 ²⁹Si MAS n.m.r. of (a) silicalite-1, (b) TS-1 (Si/Ti = 23), (c) Al-TS-1 (Si/Ti = 24; Si/Al = 45), and (d) ZSM-5 (Si/Al = 33), respectively

Table 2 Conversion of *meta*-xylene over Al-TS-1 and ZSM-5 zeolites

Zeolite Si/Al	Al-TS-1 45		ZSM-5 33	
	1	6	1	6
TOS (h)				
<i>m</i> -xylene conversion (wt%)	22	19	27	20
<i>p</i> - <i>o</i> -Xylene ratio (<i>p</i> - <i>o</i> -Xylene)	1.7	1.8	1.6	1.7
<i>M</i> -Xylene converted (%)	96	96	95	95

Reaction conditions: H₂/*m*-xylene (mole) = 6; temp. (K) = 553; WHSV = 3.5 h⁻¹; cat. wt. = 1 g

Octahedrally coordinated Al was not observed. The near theoretical ion-exchange capacity ($K^+/AlO_2^- = 0.96$) exhibited by Al-TS-1 also indicated that almost all the Al is present in the zeolite framework.

Table 1 also compares the catalytic activity and selectivity of TS-1 and Al-TS-1 in the hydroxylation of benzene with hydrogen peroxide. The selectivity for the conversion of hydrogen peroxide to total hydroxy benzenes decreased in the order TS-1 \gg Al-TS-1 > ZSM-5. The lower conversion of benzene observed on Al-TS-1 is surprising in view of the fact that benzene hydroxylation is catalyzed by the Ti⁴⁺ in the lattice and both TS-1 and Al-TS-1 have similar Ti⁴⁺ contents. Apparently, Al³⁺ ions in the lattice are detrimental to the reaction. The observed low conversion of benzene is probably due to the rapid decomposition of H₂O₂ on the Brønsted acid sites present in Al-TS-1. This is further supported by the low conversion of benzene on ZSM-5. TiO₂ (both amorphous and crystalline) was also inactive for this reaction.

Al-TS-1 exhibits significant catalytic activity and shape selectivity in *meta*-xylene isomerization (Table 2), demonstrating the presence of Brønsted acid sites (due to the incorporation of Al in the framework). In

fact, its activity is nearly the same as that of ZSM-5 on an equivalent Al³⁺ basis. As expected, the pure titanium silicate, TS-1, was completely inactive in this reaction due to the absence of acidic sites in their structure. However, interestingly, Al-TS-1 was significantly more resistant toward deactivation in the acid-catalyzed reaction vis-à-vis ZSM-5 (Table 2). The loss in activity observed in the case of Al-TS-1 is only 3%, while it is 7% in the case of ZSM-5.

In summary, the spectroscopic (XRD, i.r., and MAS n.m.r.), ion-exchange, and catalytic measurements have demonstrated the incorporation of both Ti and Al in the MFI framework. Their dual functional catalytic activity in both acid-catalyzed and oxidation reactions is demonstrated.

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