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Synthesis, Characterization, and Catalytic Properties of a Titanium Silicate, TS-2, with MEL Structure

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A new crystalline, microporous titanium silicate with MEL topology (TS-2) has been synthesized and characterized. The TS-2 samples, with Si/Ti ratios ranging between 14 and 124 were characterized by spectroscopic (XRD, framework IR, UV-VIS), adsorption, and catalytic measurements. With the progressive increase in the Ti content (i) the unitcell parameters and volume (from XRD) increased linearly, (ii) the intensity of the characteristic IR band at 970 cm^{-1} increased, and (iii) a band around 47000 cm^{-1} appeared in the electronic spectra (UV–VIS). Quite high sorption capacities of TS-2 samples were comparable to those for silicalite-2. High catalytic activity and selectivity in the hydroxylation reactions further confirmed the presence of Ti in the framework of TS-2.

INTRODUCTION

Taramasso et al. (*1*) were the first to claim the direct synthesis of a crystalline, microporous titanium silicate, TS-1 with the MFI structure, confirming the predictions given by Barrer (*2*) on the basis of theoretical arguments. Since then, a numbers of papers have reported the synthesis (*3*, *4*) characterization (*3*, *5*), and catalytic properties (6–11) of TS-1 molecular sieves. In recent years the use of TS-1 for the preparation of organic fine chemicals has enlarged the domain of zeolite catalysis. The Ti-rich TS-1 molecular sieves (Si/Ti = 10) have also been synthesized and characterized (*4*). Recently, we announced the synthesis of a new titanium silicate, TS-2, with MEL topology (*12*). In the present paper we now report the details of the synthesis and characterization of this new titanium silicate, TS-2. The characterization of the TS-2 has been carried out using various spectroscopic (such as XRD, IR, UV–VIS) as well as adsorption and catalytic methods.

EXPERIMENTAL

Synthesis

In a general procedure for the synthesis of TS-2, the required amount of a methanolic solution of tetrabutyl ammonium hydroxide, TBA–OH (20 wt%, Aldrich) was added to the calculated amount of tetraethyl orthosilicate (TEOS, Aldrich) in order to hydrolyze the latter. To the resultant clear liquid mixture, a solution of required quantity of titanium tetrabutoxide ($Ti(OBu)_4$), in *dry* isopropyl alcohol was added dropwise under vigorous stirring. The clear liquid thus obtained was stirred for about 30 min in order to complete the hydrolysis of TEOS and $Ti(OBu)_4$. Finally, the required amount of doubly distilled water was added to the above mixture. This final mixture was stirred at 348–353 K for about 1–2 h to remove the alcohol. The molar chemical composition of the reaction mixture at this stage was: 0.2 TBA–OH : SiO_2 : $xTiO_2$: 20 H_2O, where x was varied in the range of 0.14–0.0055. The crystallization was done statically at 443 K for 2–7 days depending upon the Ti content in the reaction mixture. The crystalline solid was filtered, washed with deionized water, dried at 373 K for

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TABLE 1

Si/Ti Molar Ratios of TS-2

Sample	Si/Ti molar ratio		Crystallization time, days
	Gel	Product	
A	180	124	2
B	95	70	2
C	65	48	2
D	33	27	3
E	17	21	4
F	7	14	8
Si-2[a]	>3000	>3000	2

[a] Si-2, silicalite-2.

6–8 h, and calcined at 823 K for 16 h in dry air. The organic free TS-2 samples were treated with ammonium acetate solution (6 wt%) and calcined before using them as catalyst.

Characterization

The characterization of the sample was carried out using XRD (Regaku MAX 3D, Cu$K\alpha$), framework IR spectroscopy (Perkin–Elmer 221), UV–VIS reflectance spectrometry (PYE Unichem SP-8-100), and adsorption (Cahn balance) methods. The chemical analyses were obtained by ICP (John Yvon JYU-38 VHR) and XRF (Regaku, 3070). The catalytic runs were carried out batchwise. The products were analyzed by high-resolution capillary GC (HP 5889).

RESULTS AND DISCUSSION

Synthesis

The synthesis of titanium–silicate-2 (TS-2) with varying Si/Ti molar ratios and pure silicalite-2 was done under similar conditions. Alkalimetal hydroxides (e.g., NaOH, KOH) were not added deliberately to the synthesis mixture as it is known (*2–5*) that the presence of alkali metal in the gel is unfavorable for the incorporation of Ti in the zeolite framework.

The use of alcohol (e.g., isopropanol in the present case) favors the miscibility of TEOS and $Ti(OBu)_4$ solutions and inhibits the instantaneous hydrolysis of Ti-alkoxide, before its combination with reactive silica species. It is known that for the optimum and reproducible synthesis of titanium silicates, the formation of white TiO_2 should be avoided (2–5) because once the TiO_2 is formed the Ti incorporation into the framework is inhibited. Further, it is our experience (*4*) that for the efficient synthesis of Ti-

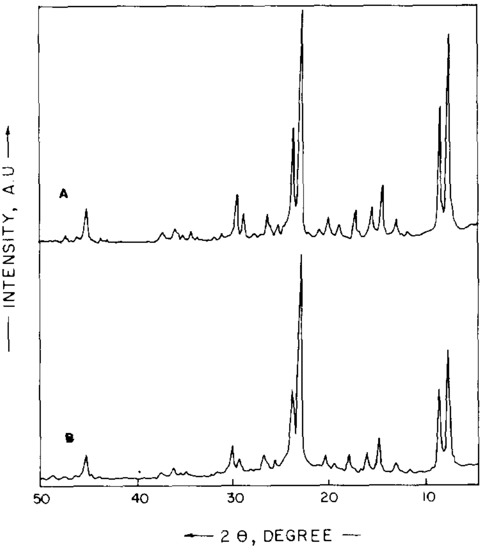

FIG. 1. X-ray powder patterns of calcined samples of silicalite-2 (A) and TS-2 sample D (B).

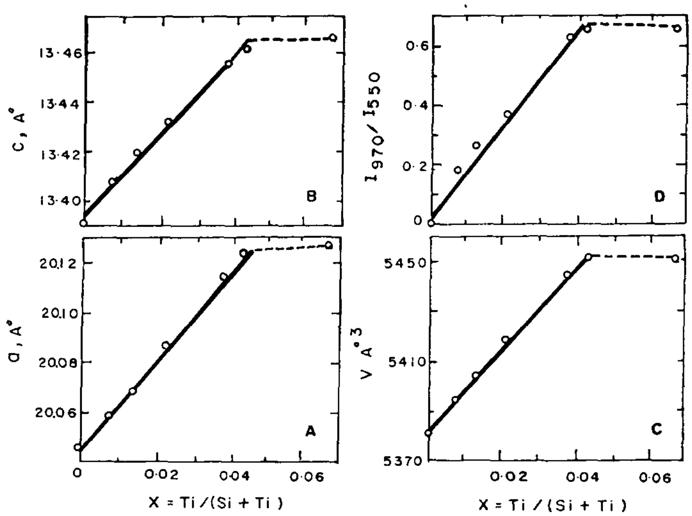

FIG. 2. The unit cell parameters *a* (A), *b* (B), volume *V* (C), and ratio of intensities of 970/550 cm^{-1} IR bands (D) vs mole fraction of titanium (*x*) in various TS-2 samples.

rich silicates, the relative rates of hydrolysis of Si-alkoxide (preferably of lower molecular weight) and Ti-alkoxide (preferably with higher molecular weight) should be matched as closely as possible. Since the hydrolysis of Si-alkoxides is much slower than that of the Ti-alkoxides and the rate of hydrolysis decreases with increasing chain length of a particular alkoxide (*13*, *14*), Ti-butoxide was used in our studies instead of the conventional Ti-ethoxide as a source of Ti.

Characterization

X-ray diffraction. The Si/Ti molar ratios of both the reaction mixture and the crystalline product of all the samples investigated here are given in Table 1. The XRD pattern of a representative TS-2 (sample D) (Fig. 1A) matched well with that of Silicalite-2 (*15*) (Fig. 1B). Both silicalite-2 and TS-2 possess tetragonal symmetry. The replacement of Si by the larger Ti^{4+} ions, in the framework, causes an increase in the lattice parameters and hence unit cell volume (*2–5*). Figure 2 (A–C) depicts a regular increase in the unit cell parameters: *a*, *c*, and volume (*V*) with the increase of Ti content of the TS-2. This is consistent with the incorporation of larger Ti^{4+} ions in the silicalite-2 structure. The deviation in the case of sample F (Si/Ti = 14) is quite significant indicating that not all the Ti in sample F is incorporated into the framework. This fact is more clearly illustrated in Fig. 3, where the XRD patterns of the samples E and F, both calcined at 823 and 1073 K, are compared. The sample F calcined at 823 and 1073 K exhibited an enhancement in the intensity of the peak at $2\Theta = 25.4°$ (Fig. 3, curves A and B, see shaded area), characteristic of crystalline TiO_2 (anatase). After calcination at 1073 K, the intensity of the peak at $2\Theta = 25.4°$ further increased (curve A). However the sample E did not show such an enhancement (Fig. 3, curve C and D). These results clearly demonstrated the presence of extra-lattice Ti in sample F. The maximum incorporation of Ti in the TS-2, achieved during the present study, amounted to Si/Ti = 21 (sample E). In TS-1, however, still more Ti (Si/Ti ≈ 10) could be incorporated (*4*).

Framework IR. Figure 4 illustrates the framework IR spectra of samples A–D. An absorption band at 970 cm^{-1} has been observed in the case of all TS-2 samples. The intensity of this band increases with the Ti content of the TS-2. Similar observations have also been reported in the case of TS-1

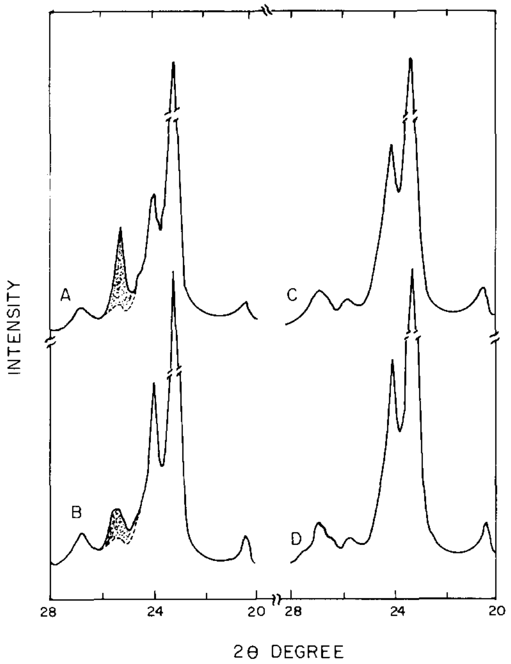

FIG. 3. X-ray powder patterns of samples E and F, calcined at 1073 K (curves A and C) and at 823 K (curves B and D). The shaded area represents the enhancement of the intensity of XRD peak at $2\Theta = 25.4°$ in sample F (curves A and B).

(2–11, 10, 15). In Fig. 2D the ratio of intensities of the IR bands at 970- and 550-cm^{-1} band (the latter being characteristic of the MEL structure) is plotted against the Ti content of the calcined TS-2 sample. An increase in the value of this ratio with that of Ti content in TS-2 (except for sample F) suggests a direct relation between the presence of Ti in the framework and 970-cm^{-1} IR band. No such band was observed in the IR spectra of silicalite-2 which was synthesized under identical conditions. Again a deviation in the case of sample F (Fig. 2D), indicates the presence of some extralattice Ti in sample F (see unit cell data also, Fig. 2 A–C). This 970-cm^{-1} band has been assigned, in accordance with the assignment of 960- to 970-cm^{-1} IR band in TS-1 molecular sieves by Boccuti et al. (*5*), to the stretching mode of a $[SiO_4]$ unit bonded to a Ti^{4+} ($O_3Si–O–Ti$) ion in the $[SiO_4]$ structure. Based on detailed IR studies of amorphous and crystalline silicalite-1 and titanium silicate (TS-1), Thangaraj et al. (*4*) had concluded that although the presence of the 950- to 970-cm^{-1} band in the IR spectrum of the as-synthesized Ti-containing molecular sieves (TS-1) may not be taken as evidence of the incorporation of Ti in the framework, it may be a consequence of such an incorporation.The retention of this band in the *calcined* titanium–silicate further supports the incorporation of Ti in the framework.

UV-VIS spectroscopy. Figure 5 depicts the diffuse reflectance spectra of TS-2 (sample D) and silicalite-2. TS-2 exhibited a strong band at around 212 nm (≈47000 cm^{-1}), pure silicalite-2 did not show such a signal at all. The crystalline TiO_2 (anatase),

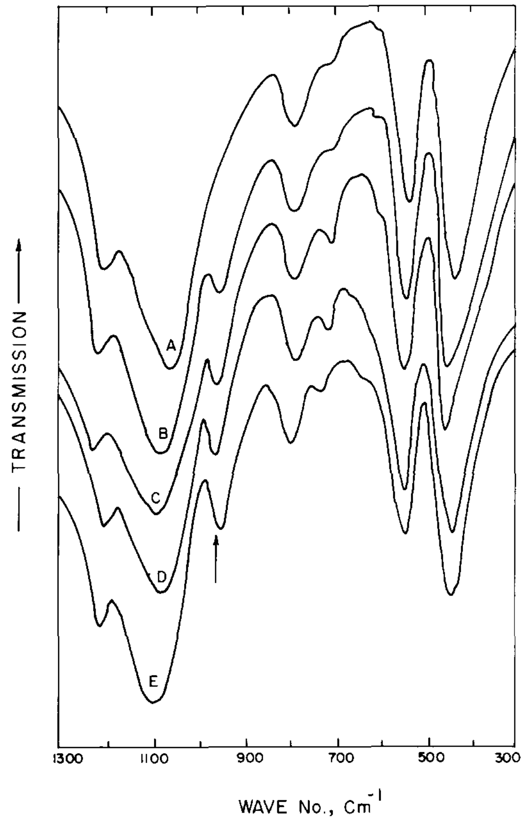

FIG. 4. Framework IR spectra of silicalite-2 (curve A) and TS-2 samples A, B, D, and E (curves B–E, respectively).

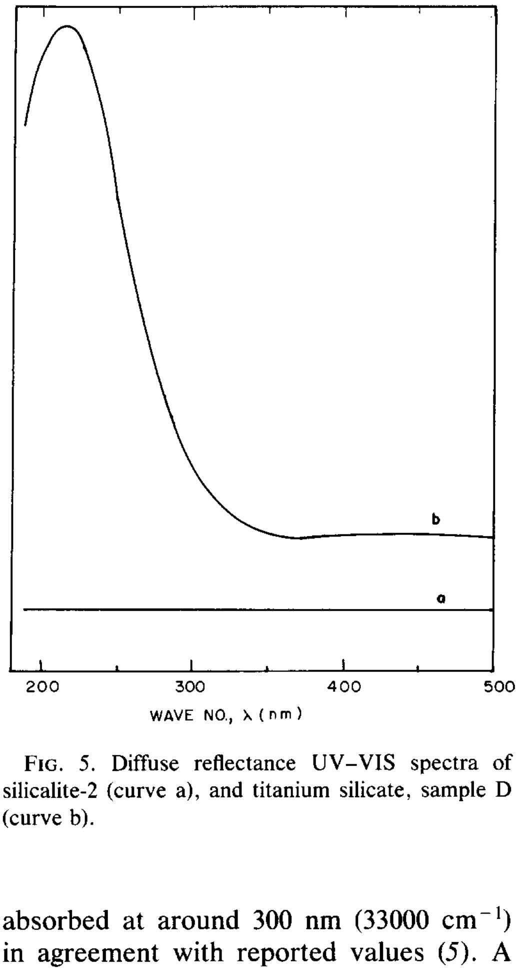

FIG. 5. Diffuse reflectance UV–VIS spectra of silicalite-2 (curve a), and titanium silicate, sample D (curve b).

absorbed at around 300 nm (33000 cm^{-1}) in agreement with reported values (*5*). A similar absorption around 212 nm had also been observed in UV–VIS spectrum of titanium silicalite-1 with MFI structure, TS-1 (*4*, *5*). This absorption around 212 nm is attributed (*4*, *5*, *16*) to a charge transfer from oxygen to empty *d* orbitals of Ti^{4+} ions.

Adsorption. In Table 2 the adsorption capacities (at $P/P_0 = 0.5$ and $T = 298$ K) of silicalite-2 and TS-2 (samples D, E, and F calcined at 823 and 1073 K) for *n*-hexane and cyclohexane are recorded. TS-2 exhibited sorption capacity comparable to that of silicalite-2. Sample F exhibited lower adsorption capacity probably due to the presence of some occluded matter. After the calcination at 1073 K adsorption capacity of sample F decreased quite significantly, probably due to partial blocking of the pores by occluded crystalline TiO_2 (anatase) (also see Figs. 2 and 3). However, samples D and E did not show any change in sorption capacities after calcination at 1073 K.

Catalysis. The catalytic activity and selectivity of TS-2 (sample D) in the hydroxylation of phenol, anisole, toluene and benzene with hydrogen peroxide (26 wt% aq.) are given in Table 3. The catalytic activity of sample D, treated at 1073 K is also included. The significant catalytic activity of TS-2 sample in the hydroxylation reactions indicates the presence of active Ti species in the zeolite framework. The fact that the catalytic activity of titanium silicate molecular sieves in the hydroxylation reactions originates from framework Ti (*3*, *4*, *6*, *7*) is further confirmed by complete inertness of Silicalite-2 (Si-2), TiO_2 (both amorphous and crystalline), amorphous titanium silicate, and physical mixtures of Silicalite-2 and TiO_2 (both amorphous and crystalline) in this reaction.

In Fig. 6 the product distribution and H_2O_2 selectivity (i.e., conversion of H_2O_2 into dihydroxy benzenes) in the hydroxylation of phenol by H_2O_2 are plotted against reaction time. H_2O_2 selectivity increases with the reaction time and stabilizes around 80% (mole) after 25 h. The activity of sample D treated at 823 K and 1073 K was similar (Table 3) indicating the stability of framework titanium even at 1073 K. The catalyst could be regenerated many times without any significant loss in activity.

CONCLUSIONS

1. A new titanium silicate with the MEL (ZSM-11) structure has been prepared. The maximum titanium incorporation achieved amounted to a Si/Ti ratio of 21.

2. Evidence for the presence of Ti in the framework of MEL was obtained from XRD (a regular increase in the unit cell parameters with Ti content), framework IR spectroscopy (an increase in the intensity of 970 cm^{-1} band with Ti content), UV–VIS spectroscopic techniques, and its non-acidic catalytic behavior in the hydroxylation of aromatics.

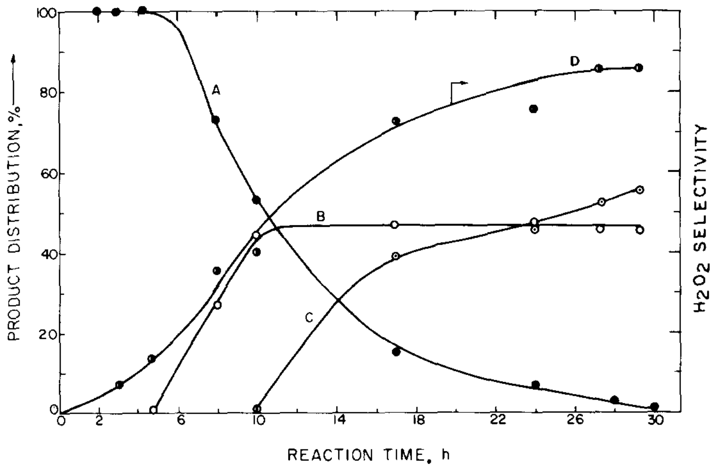

FIG. 6. Hydroxylation of phenol, product distribution, and H_2O_2 selectivity as a function of reaction time. (A) *p*-benzoquinone, (B) catechol, (C) hydroquinone, (D) H_2O_2 selectivity.

TABLE 2

Adsorption Properties of TS-2 (P/P_0 = 0.5; = T 298 K)

Temp. (K)[a]	Si-2		Sample D		Sample E		Sample F	
	823	1073	823	1073	823	1073	823	1073
n-Hx	12.4	—	14.4	14.3	13.1	12.7	12.5	8.8
c-Hx	6.5	—	8.9	9.2	9.2	8.3	5.6	1.3

[a] Calcination temperature; *n*-Hx, *n*-hexane: *c*-Hx, cyclohexane.

TABLE 3

Catalytic Properties of TS-2 Catalyst (Sample D) in Hydroxylation of Various Aromatic Compounds with H_2O_2 (Reaction Temp. = 55 K, Time = 24 h, Solvent, Acetone)

Reactant	Feed ratio[a]	H_2O_2 Conv. wt% (into hydroxy prod.)	Hydroxy products[b]				
			ortho	*meta*	*para*	PBQ	Ph
Phenol	33	78.3	51.5	—	48.3	6.5	—
Phenol[c]	33	40.0	40.0	—	60.0	—	—
Phenol[d]	33	76.5	45.9	—	49.5	4.6	—
Anisole	33	81.0	32.1	67.9	—	—	—
Toluene	10	53.5	39.3	0.8	59.9	—	—
Benzene	10	57.0	—	—	—	33.6	66.4

[a] Molar ratio (reactant/$H_2O)_2$) *100.
[b] PBQ, *para*-benzoquinone; Ph, phenol.
[c] Solvent, methanol.
[d] Over sample D treated at 1073 K for 2 h.

3. Titanium in tetrahedral framework positions was stable even at 1073 K; this is supported by the similar catalytic activity, adsorption capacity, and ratio of the intensities of the 970/550 cm^{-1} IR bands for samples treated at 823 and 1073 K.

4. The non-acidic catalytic properties of TS-2 in the hydroxylation of aromatic compounds indicated the presence of Ti in the framework of MEL structure. TS-2 samples can be regenerated many times without any significant loss of catalytic activity.

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