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Catalytic Properties of Crystalline Titanium Silicalites

I. Synthesis and Characterization of Titanium-Rich Zeolites with MFI Structure

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Crystalline titanium silicalites with the MFI structure and high titanium content (Si/Ti=10) have been prepared using improved synthesis procedures. The monoclinic lattice symmetry of silicalite-1 changes to orthorhombic on introduction of titanium. The titanium silicalites retain their orthorhombic symmetry even after calcination in air. On progressive incorporation of titanium, (i) the unit cell dimensions and volume (from XRD) increase linearly, (ii) the crystal size decreases progressively, (iii) the intensity of the framework IR band at 960 cm^{-1} increases, (iv) a band around 47000 cm^{-1} appears in the electronic spectra due to charge transfer transitions involving Ti(IV) sites, (v) the hydrophilicity of the zeolite (from water adsorption measurements) increases, (vi) the adsorption capacity for cyclohexane increases, (vii) the ^{29}Si MAS NMR lines exhibit progressive broadening, and finally (viii) the catalytic activity in the hydroxylation of phenol to catechol and hydroquinone also increases markedly. Based on these observations, it is concluded that a significant fraction of titanium in these samples is situated in framework positions. The catalytic properties of these well-defined titanium-modified zeolites will be described in more detail in the subsequent parts of this series.

INTRODUCTION

The physicochemical and catalytic behavior of zeolites can be modified by changing their framework composition (*1*). The advent of crystalline titanium silicas with zeolitic properties has enlarged the domain of zeolite catalysis in hydroxylation and oxidation reactions (*2–8*). The substitution of Si by Ti in the MFI structure (TS-1) was first claimed by Taramasso *et al.* (*2*). We have recently reported the direct synthesis of titanium silicalite-2, TS-2, with MEL topology (*3*). A number of papers (*4–8*) have recently reported the novel catalytic properties of these crystalline titanium silicalites. However, a systematic detailed description of preparation of well-characterized samples of these materials and correlations between their physicochemical and catalytic properties has not been published. During our earlier studies (*3, 8*), we had observed that the catalytic activity of these materials can be enhanced by increasing their titanium content. The original investigators of TS-1 had reported (*2, 4, 5*) a minimum value of Si/Ti of only 39 for the incorporation of Ti in the MFI structure.

In the present series of papers we describe the synthesis, characterization, and catalytic properties of titanium-rich (Si/Ti values up to 10) zeolites with MFI and MEL structures. This paper (Part I) deals with titanium silicalites possessing the MFI structure. Part II will describe their catalytic performance in the conversion of phenol to hydroquinone and catechol.

EXPERIMENTAL

A general procedure for the preparation of crystalline titanium silicalites is given below: To a solution of tetraethyl orthosilicate (TEOS), in isopropyl alcohol, the appropriate amount (almost one-half of the stoichiometrically required quantity) of aqueous tetrapropyl ammonium hydroxide (20% aq. TPAOH solution, Aldrich) was added to partly hydrolyze the TEOS. To this resultant liquid mixture, a solution of the re-

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quired quantity of titanium tetrabutoxide $Ti(OBu)_4$, in *dry* isopropyl alcohol was added dropwise under vigorous stirring. The clear liquid was stirred for about 1 h in order to complete the hydrolysis of TEOS and $Ti(OBu)_4$. Finally, the solution of remaining TPAOH in doubly distilled water was added slowly to the above mixture. This final mixture was stirred at 348–353 K for about 3–6 h to remove the alcohol. The chemical composition of the initial gel is given in Table 1. The crystallization was done statically at 443 K for 1–5 days. The crystalline solid thus obtained was filtered, washed with distilled water, dried, and calcined at 823 K in air for 10 h. The above material was further treated with 10% aqueous ammonium acetate solution twice at 363 K for 5 h and recalcined in air at 823 K for 10 h. Silicalite-1 used in the present study was also synthesized under identical conditions except that the titanium source was not added.

The characterization of the samples was carried out using XRD (Philips, PW-1710 $CuK\alpha$), framework IR spectroscopy (Perkin–Elmer 221), UV–VIS reflectance spectrometry (Pye Unichem SP-8-100), MAS NMR (Bruker MSL-300), optical microscopy, and adsorption (McBain balance) techniques. The chemical analyses were obtained by ICP (John Yvon JYU-38 VHR). Titanium was also analyzed by colorimetry. The catalytic runs were carried out batchwise (*3*, *8*). The products were analyzed by high-resolution capillary gas chromatography (HP 5889).

RESULTS AND DISCUSSION

Synthesis

The results of the synthesis of various titanium silicalite samples A–F are recorded in Table 1. The Si/Ti ratios in the starting gel as well as the final zeolite are also given therein. All the samples were highly crystalline and phase-pure. Microscopic examination confirmed the absence of amorphous matter *outside* the zeolite pores.

TABLE 1

Si/Ti Molar Ratios of the Titanium Silicalite Zeolites[a,b]

Sample	Si/Ti molar ratio		Crystallization time (days)	Crystal[c] size (μm)
	Gel	Crystalline product		
S–1[d]	—	—	3	2.0–3.0
A	160	99	3	0.5–1.0
B	66	46	3	0.4–0.8
C	33	23	4	0.5–1.0
D	24	17	4	0.5–1.0
E	14	10	6	0.3–0.8
F	10	07	5	0.3–0.8

[a] Molar composition of gel (after removing alcohol): 0.36 TPAOH; 0.007–0.10 TiO_2; SiO_2; 20 H_2O.

[b] All the crystallizations were conducted at 443 K.

[c] The crystals of all the samples were cuboid in shape.

[d] S–1 corresponds to silicalite-1.

The maximum mole fraction of titanium (x) in the TS-1 zeolites reported in the literature so far (*2*, *4*, *5*) is 0.025 (corresponding to a Si/Ti molar ratio of 39), even though in the starting gel Si/Ti ratios as low as 5 had been used. In order to incorporate more titanium in the TS-1 framework, we had modified the synthesis procedure in two ways. First, the titanium alkoxide was dissolved in *dry* isopropyl alcohol to avoid its instantaneous hydrolysis to stable TiO_2 resulting in the poor incorporation of Ti. Second, titanium tetrabutoxide was used as the source of titanium instead of the conventional titanium tetraethoxide because the hydrolysis of the former is slower. The formation of stable titanium oxide and alkali metal titanates must be avoided (*2–4*, *8*). It is our experience that for the efficient incorporation of Ti in the zeolite framework, the relative rates of hydrolysis of Si alkoxide (preferably of lower molecular weight) and Ti alkoxide (preferably with high molecular weight) should be matched as closely as possible. This method of synthesis provided TS-1 samples with higher Ti content (Table 1). Further, the synthesis time was also reduced considerably (1–5 days at 433 K com-

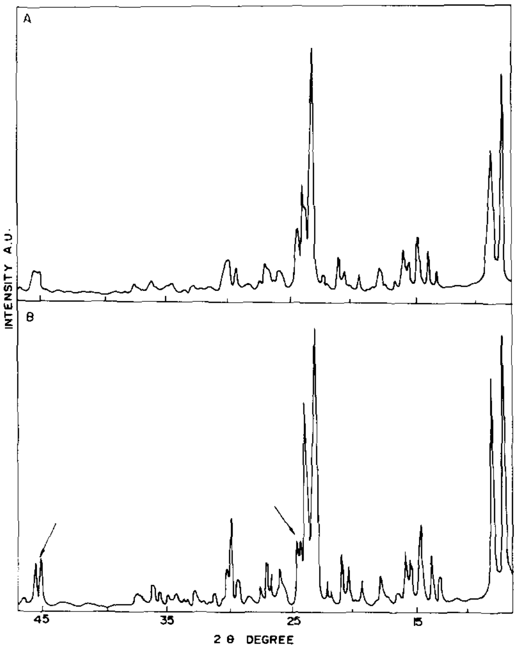

FIG. 1. X-ray powder patterns of calcined samples of silicalite-1 (B) and sample C (A).

pared to 6–30 days at 448 K (*2*)). The pH of the final reaction mixture (liquid or gel) ranged between 12.5 and 12.8. No Ti was detected in the mother liquor after the filtration of crystalline product. However, dissolved,unreacted silica was present. The quite high pH may be responsible for this phenomenon, explaining loss of Si during the hydrothermal crystallization of TS-1 molecular sieves.

Characterization

X-ray diffraction. The aluminum content, as an impurity, in our titanium silicalite samples was very low (Si/Al > 2000). The X-ray diffraction powder pattern of the calcined TS-1 zeolites was similar to that of ZSM-5 zeolites. The symmetry of the calcined TS-1 was orthorhombic (Fig. 1A). As expected, calcined silicalite-1 had monoclinic symmetry (Fig. 1B). The persistence of the orthorhombic symmetry even in the calcined state in the titanium silicalites is indicative of the location of Ti in the zeolite framework (*2*).

TABLE 2

Unit Cell Parameters and Symmetry of Calcined Samples of Silicalite-1 (S–1) and Titanium Silicalites

Sample	x^a	Unit cell parameters (Å)			Symmetry^b
		a	*b*	*c*	
S–1	0.000	20.087	19.885	13.381	M
A	0.010	20.092	19.889	13.385	O
B	0.021	20.066	19.897	13.399	O
C	0.042	20.102	19.910	13.370	O
D	0.056	20.090	19.955	13.430	O
E	0.091	20.090	19.955	13.461	O
F	0.125	20.128	20.003	13.470	O

^{a} x = Ti/(Ti + Si).

^{b} M, monoclinic; O, orthorhombic.

The replacement of Si by the larger Ti ions in the tetrahedral zeolite framework causes a slight expansion in the unit cell parameters (Table 2) and volume (*1*, *2*). In Fig. 2 the unit cell volume calculated for various TS-1 samples is plotted against their titanium content. A linear increase in the unit cell volume, *V*, with the increase in the mole fraction of Ti (x= Ti/Si + Ti) suggests the presence of titanium in the framework. However, the deviation in the case of sam-

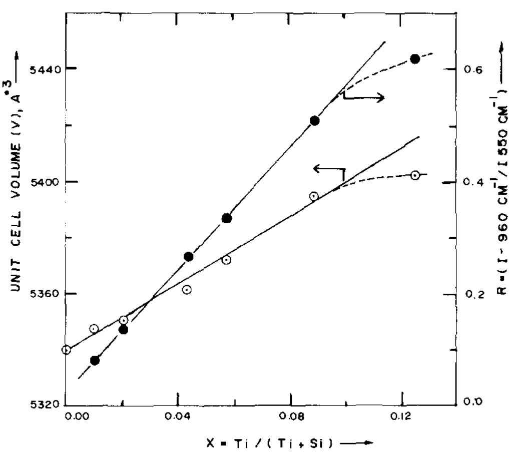

FIG. 2. The unit cell volume (—○—) and ratio of intensities of 960/550 cm^{-1} bands (—●—) vs mole fraction of titanium (x) in various TS-1 samples.

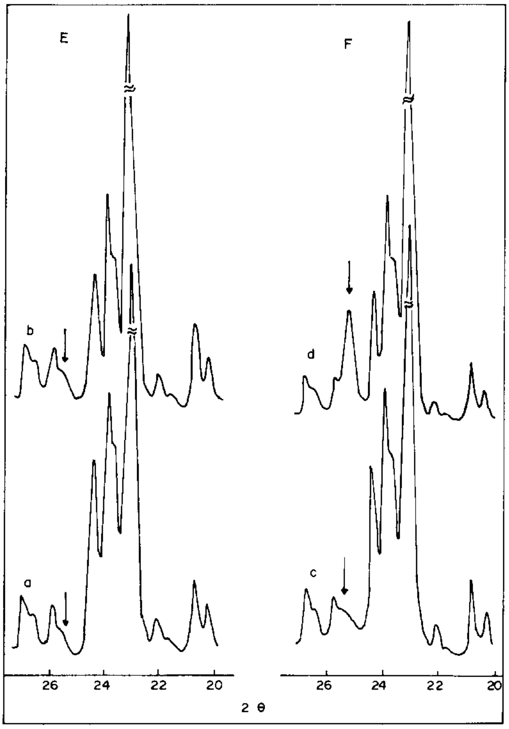

FIG. 3. X-ray powder patterns of samples E and F, calcined at 823 K (curves a and c) and at 1073 K (curves b and d).

ple F(x = 0.125) is quite significant indicating that not all the Ti in sample F is present in the framework. The XRD patterns of samples E and F calcined in air at 823 and 1073 K, respectively, are compared in Fig. 3. After calcination at 1073 K the XRD pattern of sample F exhibits a new peak around 2θ = 25.4°, characteristic of crystalline TiO_2, anatase (*9*). There was no such change in the XRD pattern of sample E. These observations suggest the presence of extralattice titanium in sample F. Similar conclusions are also drawn from framework IR spectroscopy, adsorption, and catalytic studies discussed later.

Framework IR spectroscopy. Figure 4 illustrates the framework IR spectra of calcined silicalite-1 and TS-1 samples. An absorption band at 960 cm^{-1} has been observed in the case of all TS-1 samples. The relative intensity of this band also increases with Ti content. Similar observations have also been reported by others (*2, 4–7, 10*). The ratio of the intensities of the 960 to 550 cm^{-1} bands (the latter being characteristic of the MFI structure) increases with the Ti content of the zeolite (Fig. 2). The 960 cm^{-1} band was not observed in the IR spectra of calcined silicalite-1 synthesized in the absence of titanium under otherwise identical conditions. Taramasso *et al.* (*2*) and others (*3–5, 7*) have attributed this 950–970 cm^{-1} band to Ti incorporation in the zeolite framework. Kraushaar and Van Hoof (*10, 11*) also observed the appearance of a new band at 970 cm^{-1} when they incorporated Ti in the framework of highly dealuminated ZSM-5 zeolites via vapor phase $TiCl_4$ treatment. Skeels and Flanigen (*12*), on the other hand, did not observe this band

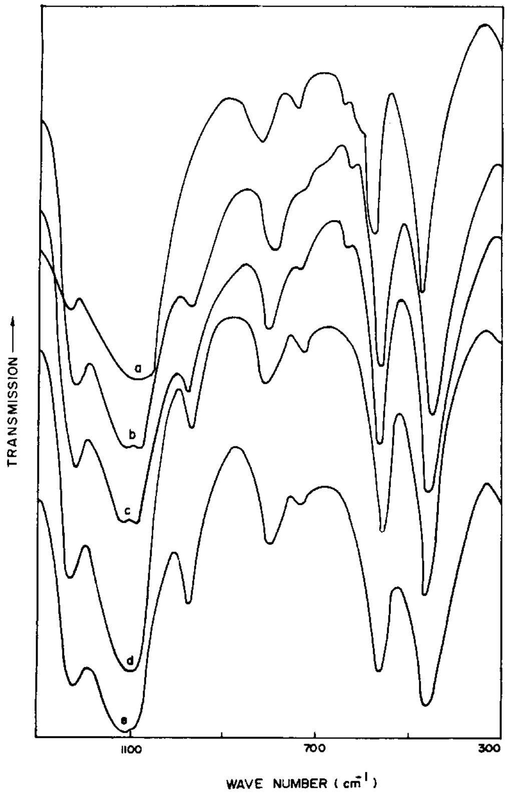

FIG. 4. Framework IR spectra of silicalite-1 (curve a) and TS-1 samples B–E (curves b–e, respectively).

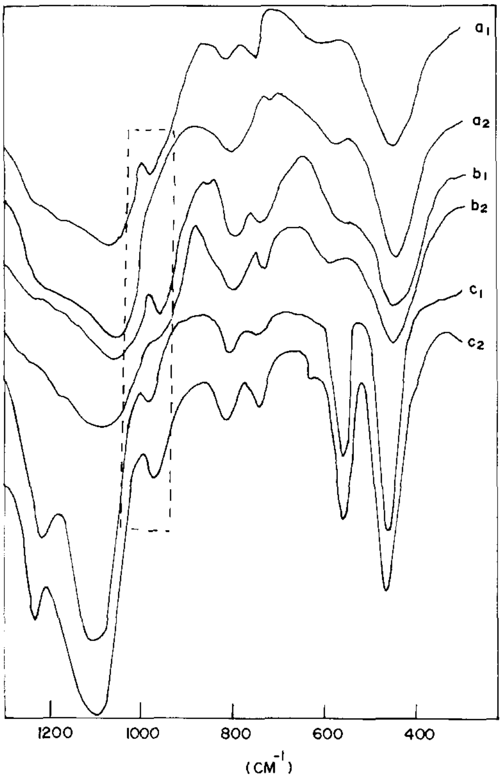

FIG. 5. Framework IR spectra: curves a_1 and b_1 refer to the amorphous gels of silicalite-1 and sample C respectively; curves a_2 and b_2 refer to the samples after calcination at 823 K in air. The spectra of crystalline TS-1 in the as-synthesized form and after calcination are shown in curves c_1 and c_2, respectively.

when Ti incorporation was done from aqueous fluorotitanate solutions. Recently, based upon detailed IR and UV-visible spectroscopic studies, Boccuti *et al.* (*7*) have demonstrated that the IR band around 960 cm^{-1} exhibited by TS-1 zeolites can also be attributed to a stretching mode of a [SiO_4] unit *bonded* to a Ti^{4+} ion (O_3SiOTi). The Ti–O–Si bond was found to be more polar than the Si–O–Si bond (*7*).

Figure 5 illustrates the evolution of the 960–980 cm^{-1} band during the preparation of silicalite-1 and TS-1. Curves a_1 and b_1 (in Fig. 5) refer to the spectra of the *amorphous* precursor gels obtained after mixing the constituents in the preparation of silicalite-1 and TS-1, respectively; curves a_2 and b_2 refer to the samples (also amorphous) obtained after calcining the respective amorphous gels in air at 823 K. Curve c_1 is the spectrum of the as-synthesized *crystalline* TS-1. Curve c_2 is the spectrum of the same sample after calcination in air at 823 K. The IR band at 960–980 cm^{-1} is present in the amorphous precursor gels of both silicalite-1 and TS-1 (curves a_1 and b_1). On calcination, this band disappeared (curve a_2) or greatly diminished in intensity (curve b_2) in the case of the amorphous precursors of silicalite-1 and titanium silicalite, respectively. However, in the case of crystalline titanium silicalite, TS-1, there was an increase in the intensity of this IR band on calcination (curve c_2). It may be recalled that calcined crystalline silicalite-1 does not exhibit the 960 cm^{-1} band (Fig. 4). The retention of the 960–980 cm^{-1} band in the *calcined* crystalline titanium silicalites may point to the presence of titanium in the zeolite framework.

UV-VISIBLE spectroscopy. Figure 6 compares the reflectance spectra of silicalite-1 and sample C. The diffuse reflectance spectrum of titanium silicalite (sample C) exhibited a strong transition around 47000 cm^{-1} (212 nm). The silicalite-

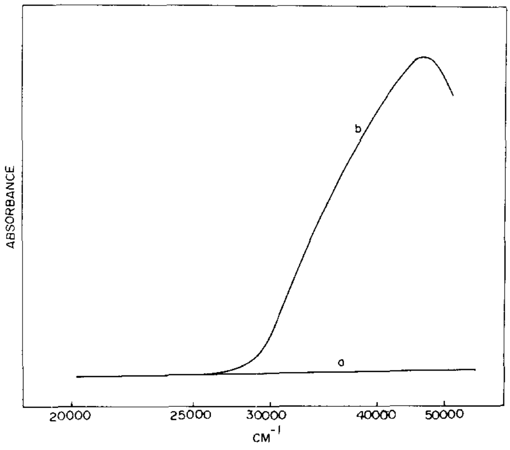

FIG. 6. Diffuse reflectance UV–VIS spectra of silicalite-1 (curve a), and titanium–silicalite, sample C (curve b).

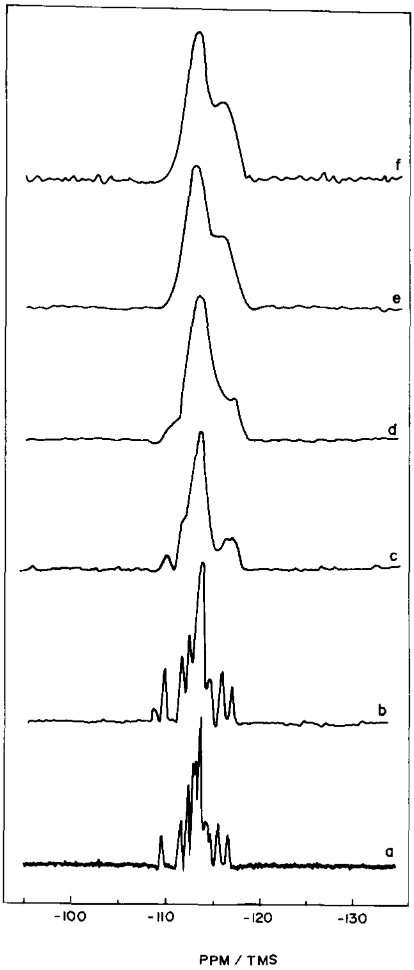

FIG. 7. ^{29}Si MAS NMR spectra of silicalite-1 (curve a) and TS-1 samples B–F (curves b–f respectively; all samples were calcined at 823 K).

1 sample did not show such a signal at all. Pure TiO_2 (anatase) absorbs at 312 nm (32000 cm^{-1}) (*13, 14*). The absence of this band in our samples further confirms the absence of occluded TiO_2 in them. Boccuti *et al.* (*7*) have also observed a transition around 48000 cm^{-1} in TS-1 and assigned (*7*) it to an electronic transition having charge transfer character involving Ti(IV) sites. The charge transfer probably occurs from the excitation of an oxygen 2*p* electron in the valence band to the empty *d* orbitals of titanium ions (*13, 14*).

^{29}Si MAS NMR spectroscopy. Figure 7 illustrates the ^{29}Si MAS NMR spectra of silicalite-1 and various TS-1 samples (calcined at 823 K). As the titanium content of the zeolite increases, the linewidths broaden progressively. Simultaneously a broad peak around $\delta = -116$ ppm develops. Similar results have also been observed by other workers (*3, 10*) in the ^{29}Si MAS NMR of TS-1 zeolites. The peak at -116 ppm had been attributed (*3, 11*) to arise from the distorted silicon environment in tetrahedra containing Si–O–Ti bonds.

Adsorption

The adsorption capacity of titanium silicalites (Fig. 8), slightly increases with the content of titanium up to a Ti/(Si + Ti) value around 0.09. This may be due to the concomitant decrease in the crystal size accompanying titanium incorporation. The high adsorption capacities of all these zeolite samples (except sample F) are indicative of the absence of occluded extra-framework material *inside* their pores. The lower adsorption volume exhibited by sample F indicates the presence of some occluded amorphous matter in its pores. This is supported by a comparison of the sorption capacity of samples E and F after calcination in air at 823 and 1073 K, respectively, for 6 h (Table 3). After the 1073 K treatment, while the adsorption capacity of sample E did not decrease at all, that of sample F decreased considerably due to partial blocking of the pores by occluded TiO_2 (see Fig. 3).

Catalysis

In Fig. 9 the catalytic activity of silicalite-1 and TS-1 zeolites for the hydroxylation of phenol in the presence of H_2O_2 into dihydroxybenzenes is plotted against the mole fraction of Ti in the zeolite. Phenol conversion increased with increasing Ti content and attained stoichiometric values around $x = 0.04$. Thereafter it remained constant up

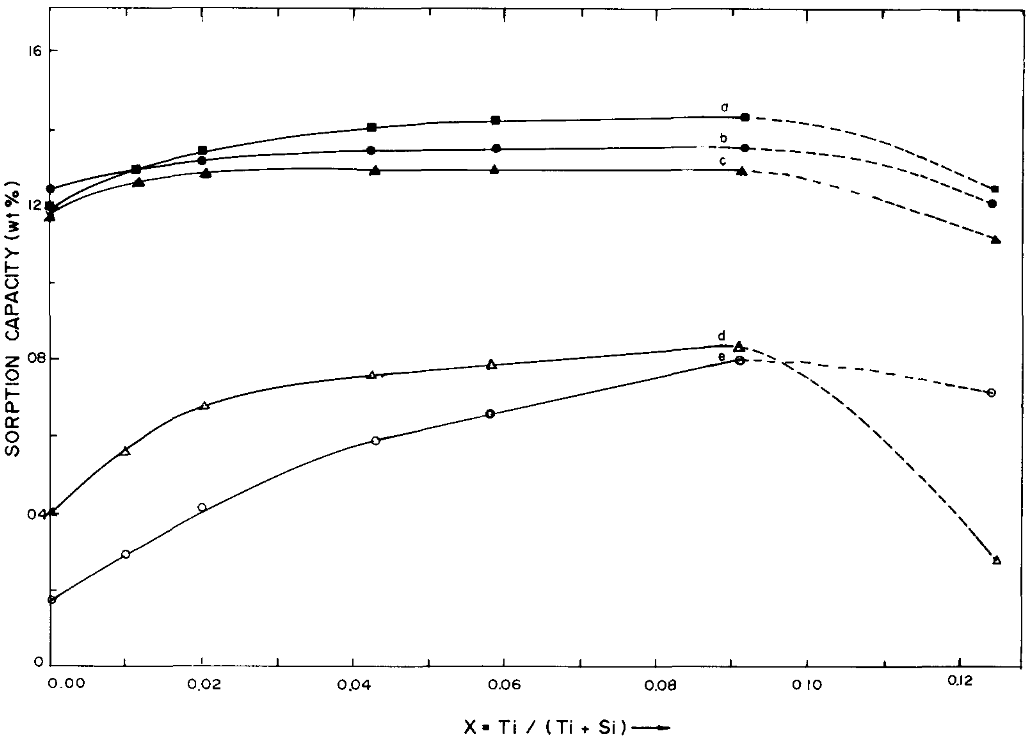

FIG. 8. Equilibrium adsorption capacities of silicalite-1 and TS-1 samples for various sorbate molecules vs molefraction (x) of Ti content in the zeolite (samples S-1, A–F). Curves a–e correspond to *n*-butylamine, *n*-hexane, benzene, cyclohexane, and water, respectively.

to x= 0.091. Sample F (x = 0.125) was less active. Pure silicalite-1, TiO_2 (both amorphous and crystalline), amorphous titanium silicates, as well as physical mixtures of silicalite-1 and TiO_2 (both amorphous and crystalline), were inactive in this reaction suggesting that titanium ions associated with the MFI framework structure are responsible for the observed catalytic activity. The exact nature of the active sites in TS-1 zeolites is still an unresolved question (*11*).

TABLE 3

Sorption Capacities (wt %) of TS-1 Samples E and F after Calcination at 823 and 1073 K for 6 h in Air (T = 298 K, P/P_0 = 0.5).

Adsorbate	Sample E		Sample F	
	823 K	1073 K	823 K	1073 K
n-Hexane	13.3	13.6	12.6	9.5
Cyclohexane	8.5	9.0	2.8	0.7

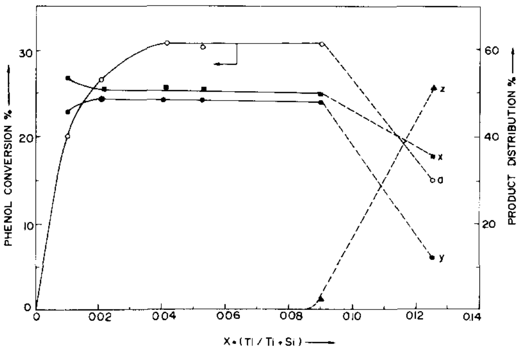

FIG. 9. Conversion of phenol vs titanium content(x) of samples (S-1, A–F). Curves a, x, y, and z correspond to phenol, catechol, hydroquinone, and *para*-benzoquinone, respectively.

CONCLUSIONS

Titanium silicalites (TS-1) with high titanium content and crystallinity have been synthesized and characterized. A modified synthesis procedure allowed us to obtain pure TS-1 samples with Si/Ti molar ratios as low as 10. Evidence for the incorporation of titanium in the zeolite framework was obtained by XRD (a regular increase in the unit cell volume) and framework IR and UV–VIS spectroscopies (appearance of bands around 960 and 47000 cm^{-1} and the dependence of their intensity on the Ti content of the zeolite). ^{29}Si MAS NMR spectra of silicalite-1 and titanium silicalite samples exhibited line broadening and a well-defined shoulder/peak around $\delta = -116$ ppm (with respect to external TMS) due to distorted Si environment, probably because of Si–O–Ti bonds. All the zeolites except sample F (Si/Ti=7) exhibited high adsorption capacities indicating the absence of amorphous matter *within* the zeolite pore system. The high catalytic activity and selectivity of TS-1 zeolites in the hydroxylation of phenol with H_2O_2 further confirmed the presence of Ti in the framework positions in our samples. Subsequent papers in this series will describe in detail the catalytic properties of these well-defined samples of titanium silicalite-1.

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