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NOTES

Framework Composition of Titanium Silicalite-1

The preparation of a titanium silicate with MFI structure (TS-1) was reported by Taramasso *et al.* (*1*) and the effective insertion of Ti in the zeolite framework was proved by structural investigations (*2*). A titanium silicate with MEL structure (titanium silicalite-2, TS-2) was obtained for the first time in our laboratories (*3*) and subsequently by others (*4*). The framework structure of TS-2 is consistent with the disordered model proposed by Perego *et al.* (*5*). These materials possess unique catalytic properties in various reactions involving hydrogen peroxide, such as the hydroxylation of phenol (*6*), the epoxidation of olefins (*7*), the oxidation of saturated hydrocarbons (*8, 9*), and the synthesis of cyclohexanone oxime (*10*). The catalytic activity of TS-1 is affected by the possible presence of extraframework Ti, which can promote extensive homolytic side reactions including decomposition of hydrogen peroxide. In the hydroxylation of phenol, this causes a variation in the distribution of isomeric products and an increase in tar production (*11*). Extraframework Ti could also be responsible for discrepancies concerning some results coming from oxidation of alkanes (compare Ref. (*12*) with Refs. (*8, 9*)).

The framework composition of TS-1 can be defined as

$$x\mathrm{TiO_2} \cdot (1 - x)\ \mathrm{SiO_2},$$

x varying between 0 and 0.025 (*2*). Attempts to produce TS-1 with $x > 0.025$ fail, since the excess titanium segregates as TiO_2 (*2*). Recently, Thangaraj *et al.* reported the possibility to produce TS-1 with higher amounts of Ti using tetrabutylorthotitanate (TBOT) instead of the ethoxy analogue (TEOT) (*13*a–c). The authors claim the synthesis of pure TS-1 samples with x up to 0.091, but the supporting data disagree with those reported in Ref. (*2*). This induced us to reconsider the problem of the characterization of TS-1, with particular attention to the determination of the real framework composition and to the evaluation of the maximum titanium content of TS-1. Among the techniques available for this purpose (XRD (*2*), IR (*2*), UV–Vis (*14*), XPS (*15*)), XRD was chosen for its effectiveness.

The unit cell parameters of TS-1 were found to increase linearly as a function of titanium content for experimental data having been obtained by least-squares fit to interplanar spacings of selected reflections in the X-ray diffraction pattern (*2*). The accuracy of the latter method is satisfactory, though it is limited somewhat by the convolution among diffraction lines present in the X-ray pattern of MFI type structures. For this reason, Rietveld analysis (*16*), which makes use of the whole profile of the diffraction pattern, was attempted. Practically, the values of atomic and thermal parameters determined by single crystal analysis for monoclinic (*17*) and orthorhombic (*18*) forms of MFI zeolites were kept fixed while refining nonstructural and unit cell parameters. The monoclinic symmetry of the crystals was easily detected by observing the splitting of some reflections in the XRD pattern (see, for example, the reflection located at $2\theta = 24.4°$ and $29.3°$).

A modified version (*19*) of the computer program PREFIN (*20*) was used for pure TS-1 samples. The software package WYRIET (*21*), a personal computer version of DBW3.2S (*22*), was used for the quantitative

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TABLE 1

List of TS-1 Samples

Sample	Reaction mixture			Reaction temp. (K)	Reaction time (h)
	SiO_2/TiO_2	$TPAOH/SiO_2$	H_2O/SiO_2		
1[a]	[b]	0.25	40	443	24
2[a]	133	0.21	40	443	24
3[a]	66	0.21	40	443	24
4[a]	100	0.25	40	443	15
5[a]	50	0.25	40	443	15
6[a]	25	0.25	40	453	15
7[a]	20	0.25	40	473	5
8[c]	14	0.36	20	443	48
9[c]	14	0.36	20	443	96
10[c]	14	0.36	20	443	168

[a] According to Refs. (*1*, *2*); Tetraethylorthotitanate as TiO_2 source.
[b] Silicalite-1.
[c] According to procedure E in Ref. (*13*a); Tetrabutylorthotitanate as TiO_2 source.

analysis of TS-1/anatase binary mixtures, in accordance with a method recently developed (*23*). More details about the strategy of the refinement will be reported elsewhere (*24*). The TS-1 samples listed in Table 1 were investigated, which include those prepared following Ref. (*13*a). Before X-ray analysis all products were calcined at 823 K, treated with an aqueous ammonium acetate solution, and further calcined. Chemical analysis of the products was made by standard methods. XRD spectra were collected stepwise on a computer-controlled Philips diffractometer, equipped with a pulse-height analyzer, in the $20° \leq 2\theta \leq 50°$ angular region, with 0.03° steps and 54-s counting time. Cu $K\alpha$ radiation (λ = 1.54178 Å) was used. With a step size of 0.03° 2θ, six to nine

TABLE 2

Crystal Data for TS-1 Samples (e.s.d.'s in Parentheses)

Sample	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	*V* (Å^3)	FWHM[a] (°)	x^b		TiO_2 wt%			(2)
							(1)	(2)	TS-1	anatase	total	
1	20.101(1)	19.877(1)	13.365(1)	90.61(2)	5339.8(8)	0.174	0	0				
2	20.104(1)	19.900(1)	13.374(1)	90.51(2)	5350.5(8)	0.186	0.005	0.005				
3	20.108(1)	19.907(1)	13.381(1)	90.55(2)	5356.0(9)	0.193	0.008	0.008				
4	20.111(1)	19.917(1)	13.385(1)		5361.2(8)	0.181	0.011	0.010				
5	20.116(1)	19.927(1)	13.394(1)		5369.1(9)	0.195	0.014	0.014				
6	20.126(2)	19.939(1)	13.412(1)		5382.1(9)	0.244	0.020	0.020				
7	20.136(2)	19.955(1)	13.420(1)		5392.3(10)	0.225	0.025	0.025				
7A[c]	20.135(1)	19.957(1)	13.418(1)		5391.8(6)	0.221	0.025	0.025				
7B[d]	20.138(2)	19.954(1)	13.419(1)		5392.2(10)	0.228	—	0.025	—	9.4	—	—
8	20.115(2)	19.934(1)	13.396(1)		5371.4(10)	0.284	0.063	0.015	1.8	3.8	5.6	7.9
9	20.114(2)	19.936(1)	13.395(1)		5371.3(10)	0.275	0.085	0.015	1.8	6.5	8.3	10.8
10	20.105(2)	19.926(1)	13.394(1)		5365.8(10)	0.258	0.119	0.012	1.4	10.8	12.2	15.1

[a] Full width at half maximum values at $2\theta = 30°$.
[b] [Ti]/([Ti] + [Si]) molar ratio; (1) from chemical analysis, (2) from XRD analysis.
[c] Mechanical mixture of sample 7 and α-Al_2O_3 (internal standard); 0.02° 2θ step size.
[d] Mechanical mixture of sample 7 and anatase (9.3 wt%).

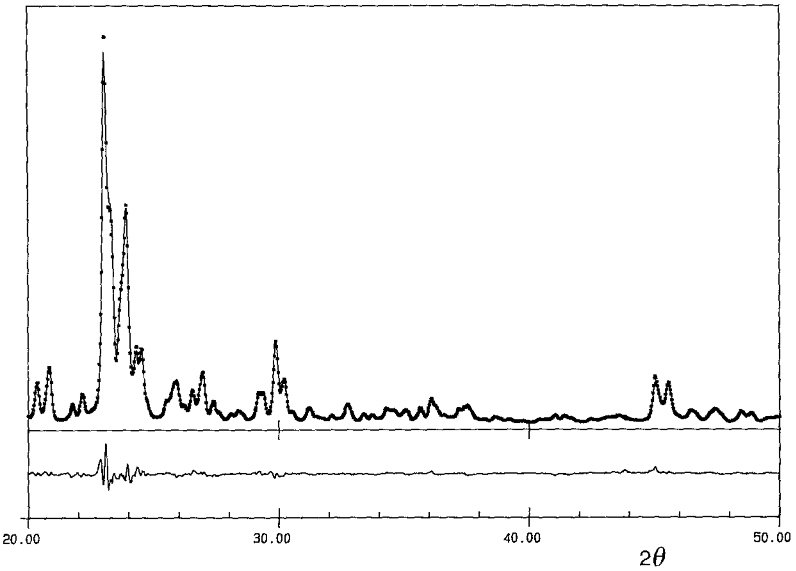

FIG. 1. Experimental (.), calculated (—), and difference (lower) trace of X-ray diffraction pattern of monoclinic silicalite-1 (sample 1).

experimental points are collected above the half height of a well separated reflection, as clearly indicated by the full width at half maximum (FWHM) values reported in Table 2. Refinements were performed by considering the contribution of both $K\alpha_1$ and $K\alpha_2$ radiation (2 : 1 intensity ratio) to the pseudo-reflection profile. The pseudo-Voigt peak profile function, with refinable gaussian contribution, was used. The diffractometer was carefully calibrated within 0.01° 2θ by using standard Si and α-Al_2O_3 calibration samples. Under this condition, we have verified the use of an internal positional standard to be unnecessary. The results obtained using a smaller step size (0.02° 2θ) and α-Al_2O_3 as an internal standard are within the e.s.d.'s with respect to those obtained by the above procedure (sample 7A, Table 2).

The results of Rietveld refinement are reported in Table 2. The fit typically obtained is shown in Figs. 1 and 2 for the case of monoclinic and orthorhombic modification, respectively.

As expected, Rietveld analysis improves the accuracy in the determination of the unit cell parameters, the standard deviation being two to three times lower than those normally obtained with the procedure used in Ref. (*2*). The linear variation of unit cell parameters previously observed has been confirmed (Fig. 3): the equations which relate them to the Ti content (x), obtained by linear regression of the data reported in Table 2, are given in Table 3. Table 3 shows the definite improvement obtained with respect to the previous data derived by least-squares fit to interplanar spacing of selected reflections (*2*).

When considering the above results, the data reported in Refs. (*13*a–c) appear quite surprising.[1] In fact, the unit cell volume reported for $x = 0.091$ (5396.5 Å^3) is very close to the value obtained for our sample 7 ($x = 0.025$, $V = 5392.3(10)$ Å^3). A possible

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[1] In Ref. (*13*a), data derived from inspection of Fig. 2 do not agree with corresponding data reported in Table 2. The discrepancy is more evident for samples C, D, and F. Furthermore, many discrepancies exist among the structural data reported in Refs. (*13*a–c), which are apparently related to the same series of samples.

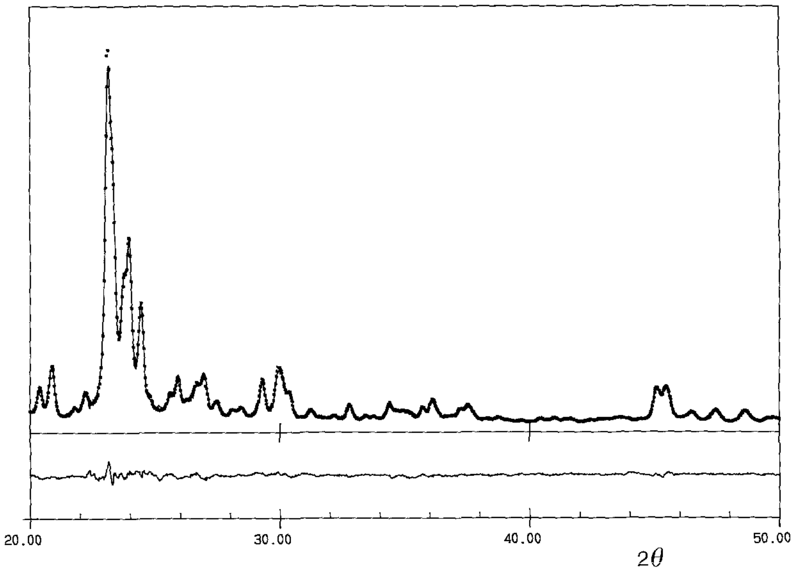

FIG. 2. Experimental (▪), calculated (—), and difference (lower) trace of X-ray diffraction pattern of orthorhombic TS-1 (sample 6).

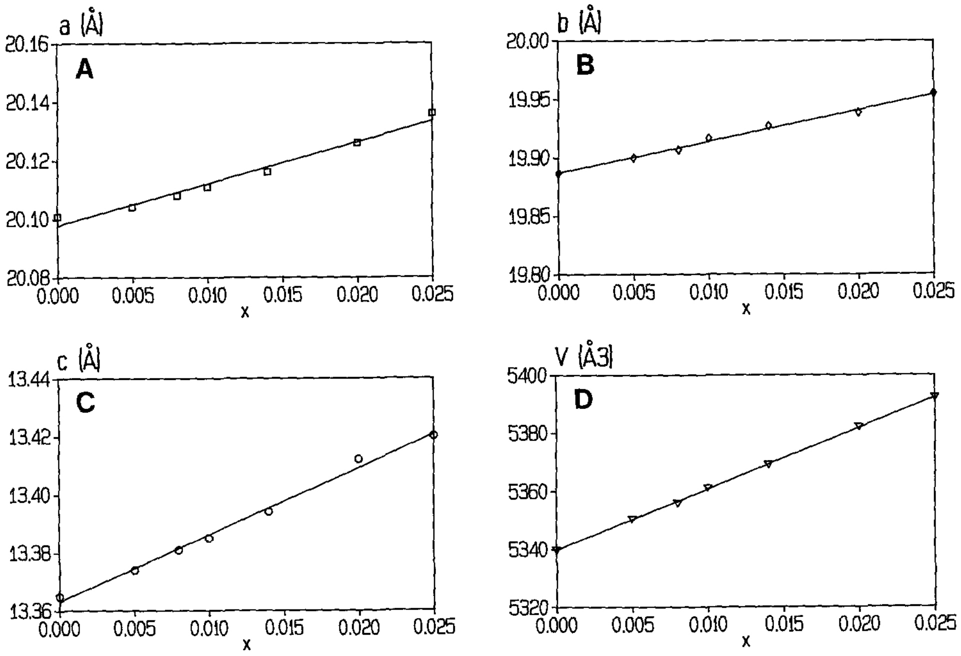

FIG. 3. Variation of *a* (A), *b* (B), *c* (C), and *V* (D) of TS-1 as a function of titanium content (x = [Ti]/([Ti] + [Si])).

TABLE 3

Linear Regression Analysis of Unit Cell Parameters[a]

	Present study			Ref. (2)		
	u	*v*	*r*	*u*	*v*	*r*
a	1.429	20.098	0.9868	0.665	20.112	0.5854
b	2.975	19.882	0.9924	2.935	19.876	0.9487
c	2.281	13.363	0.9957	2.425	13.364	0.9665
V	2110.4	5339.4	0.9993	1946	5341.8	0.9874

[a] According to the equation: $y = ux + v$; r, correlation coefficient.

explanation for the above discrepancy is that the major part of Ti in the sample of Ref. (*13*a) is segregated in an amorphous phase. As a matter of fact, when TS-1 was crystallized following the procedure described in Ref. (*13*a), TiO_2 (anatase) together with an amorphous phase (indicated by diffuse scattering in the 20°–30° 2θ region of XRD patterns, Fig. 4) was detected (samples 8–10, Table 1), even when prolonging crystallization to 7 days.

The standardless quantitative phase analysis procedure recently proposed (*23*), based on the Rietveld method, was applied to the latter samples. This method was tested on a standard mixture (9.3 wt% anatase and 90.7 wt% TS-1 sample 7, entry 7A, Table 2) obtaining a satisfactory agreement between experimental and calculated patterns (Fig. 5). The calculated values of both the anatase content (9.4 wt%) and the unit cell parameters for TS-1 agree very well with those expected (compare the results for entries 7 and 7B in Table 2). Refinement of XRD patterns of samples 8–10 converged to the values reported in Table 2. The value of

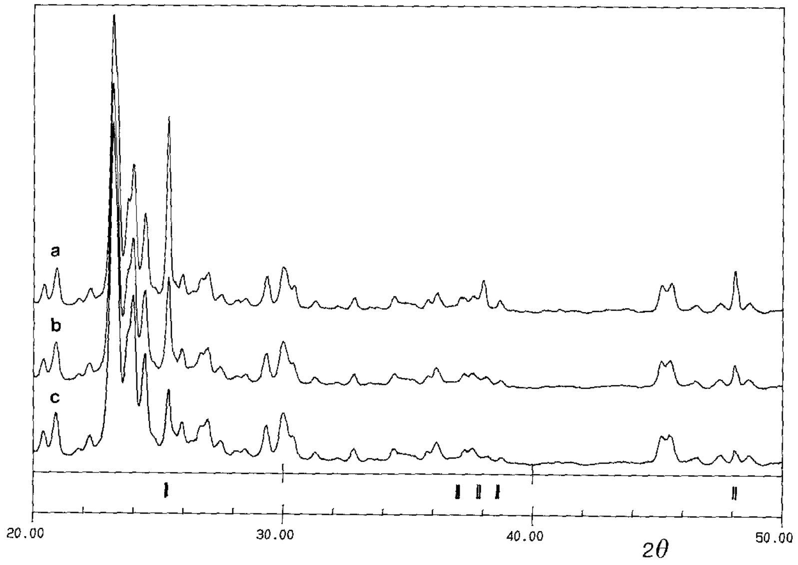

FIG. 4. X-ray diffraction patterns of calcined TS-1, sample 8 (a), 9 (b), and 10 (c), synthesized according to Ref. (*13*a). Reflections of anatase are indicated by vertical bars.

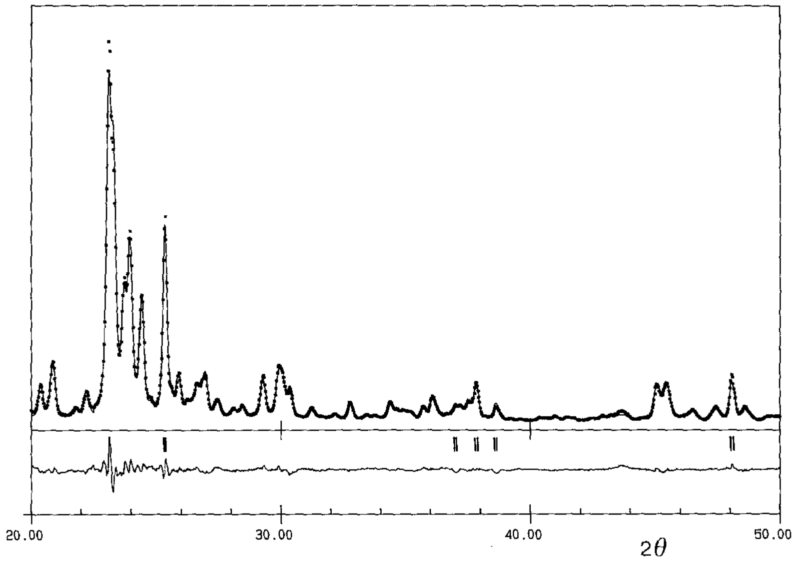

FIG. 5. Experimental (•), calculated (—), and difference (lower) trace of X-ray diffraction pattern of TS-1–anatase mixture (sample 7B). Vertical bars indicate the positions of the Bragg reflections of anatase.

framework Ti, calculated by the equation reported in Table 3, is relatively low (x = 0.012–0.015). The total amount of TiO_2 resulting from framework Ti and anatase is lower than that evaluated by elemental analysis (Table 2). This suggests that part of the titanium is probably segregated in the amorphous phase (Table 2).

In conclusion, it has been verified that the determination of unit cell parameters of TS-1 by the full-profile fitting method (Rietveld analysis) leads to more accurate results with respect to the conventional procedure which makes use of selected reflections only.

Unit cell parameters depend linearly on the atomic fraction of Ti in the framework.

The upper limit of x was confirmed to be around 0.025. Higher values claimed by Thangaraj *et al.* (*13*a–c) are evidently due to nonframework Ti.

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