

# Structural Characterization of Ti-Silicalite-1: A Synchrotron Radiation X-Ray Powder Diffraction Study

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We present high-resolution X-ray powder diffraction (XRPD) data collected at the BM16 beamline at ESRF on a set of dehydrated Ti-silicalite-1 (TS-1) samples having Ti content (molar ratio)  $x = [\text{Ti}]/([\text{Ti}] + [\text{Si}])$  in the range 0–0.022. The cell volume values resulting from Rietveld refinements of the powder diffraction data exhibit very good linear correlation ( $r = 0.99994$ ) with Ti content:  $V(x) = 2093.0x + V(0)$  [ $V(0) = 5335.8 \text{ \AA}^3$ ]. This work represents a continuation of the important characterization work of the EniRicerche group [*J. Catal.* **137**, 497 (1992)] performed on TS-1 previously treated with ammonium acetate, calcined, and measured in atmosphere (i.e., under partially hydrous conditions). Our results indicate that when XRPD measurements are performed under carefully controlled vacuum conditions a highly linear correlation between  $V$  and  $x$  is obtained without any need for sample pretreatment. Finally, the very high quality of our experimental data allows us to comment on the presence of some preferential framework T sites for Ti substitution. Such sites were recently proposed by two different groups on the basis of the results of molecular dynamics modeling. © 1999 Academic Press

## 1. INTRODUCTION

The unique efficiency yield and molecular selectivity of Ti-silicalite-1 (TS-1) (1) in catalytic oxidation reactions involving hydrogen peroxide as oxidant and in ammoxidations of ketones and aldehydes to oximes [see, e.g., the numerous papers quoted in the review articles (2, 3)], makes determination of the Ti site structure and recognition of possible preferential sites paramount in understanding the catalytic properties of this important material on a structural basis.

This is the reason for the lively debate in the literature about the structural nature of the Ti centers in TS-1: titanyl groups, extraframework defect sites, monomeric and dimeric Ti species, Ti species incorporated into edge-

sharing-type structures forming bridges across zeolite channels have been inferred by different authors; the same holds for the local geometries, where Ti species having local coordinations like tetrahedral, square pyramidal, and octahedral have been hypothesized. Now there is general consensus that the Ti(IV) atoms are incorporated as isolated centers into the framework and are substituting Si atoms in tetrahedral positions. This has been confirmed by several experimental (2–18) and theoretical (19–25) studies.

The origin of the initial confusion is probably related to the difficulty encountered in the synthesis of well-manufactured TS-1s, which requires the use of extremely pure reagents and severe control of the synthesis conditions (1). An imperfect synthesis implies incomplete incorporation of Ti into the MFI framework, leading to significant reduction in catalytic performance and, possibly, misinterpretation of structural and spectroscopic data. Moreover, the fact that only a very small amount of Ti [less than 3 wt% in  $\text{TiO}_2$ , corresponding to a molar ratio of  $x = [\text{Ti}]/([\text{Ti}] + [\text{Si}]) = 0.025$  (16)] can be substitutionally incorporated into the MFI framework (6) does not facilitate the extraction and attribution of the Ti contribution from the total experimental signal.

The assumed model of Si  $\rightarrow$  Ti isomorphous substitution is based on experimental evidence from X-ray powder diffraction (XRPD) (16), IR and Raman (7–9, 13, 14, 24), UV-vis (9, 11, 13), EXAFS (11, 12, 15, 17, 18), and XANES (11–13) results and on theoretical studies (19–25). In particular, with respect to the purpose of the present paper, we note that the XRPD measurements of Millini *et al.* (16) provided evidence that the unit cell volume of well-manufactured TS-1 previously treated with ammonium acetate increases linearly with the Ti loading of the sample. This effect can be satisfactorily explained only by assuming the insertion of Ti in framework sites.

We have three aims in the present paper: First, we confirm, with experimental data of improved quality, the linear correlation observed by Millini *et al.* (16); second, we

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TABLE 1  
Elemental and Structural XRPD Data on Investigated TS-1 Samples<sup>a</sup>

Sample	$x$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$ (°)	$V$ (Å <sup>3</sup> )	$R_{wp}$	$R_p$	FWHM (°)
/46	0	20.0693(3)	19.8806(3)	13.3731(2)	90	5335.7(2)	11.78	8.89	0.0336
/55	0.0073	20.0863(2)	19.9025(2)	13.3860(2)	90	5351.2(2)	10.40	7.72	0.0350
/68	0.0105	20.0956(1)	19.9070(1)	13.39363(9)	90	5358.0(1)	6.66	5.82	0.0372
/1	0.0152	20.1060(2)	19.9194(2)	13.4013(2)	90	5367.2(2)	10.16	7.42	0.0362
/13	0.0201	20.1170(4)	19.9350(4)	13.4100(3)	90	5377.8(3)	5.84	5.40	0.0855
/44	0.0220	20.1228(3)	19.9399(4)	13.4156(3)	90	5382.0(4)	5.67	5.20	0.0578
/46*	0	20.1085(2)	19.8854(2)	13.3816(1)	90.525(1)	5350.6(1)	9.86	7.52	0.0338
/55*	0.0073	20.1180(3)	19.9112(4)	13.3989(3)	90.286(1)	5367.2(2)	11.67	8.98	0.0392
/1*	0.0152	20.1300(3)	19.9383(3)	13.4138(2)	90	5383.8(2)	11.88	8.83	0.0382
/13*	0.0201	20.1468(8)	19.9565(8)	13.4242(5)	90	5397.3(6)	10.05	7.41	0.0831

<sup>a</sup> FWHM values were recorded at  $2\theta = 12.6342^\circ$ . Samples marked with asterisks are treated samples.

report (for the first time) that a high linear correlation can be obtained even without pretreatment of TS-1 with ammonium acetate [as recommended in Ref. (16)], providing that samples are activated under dynamic vacuum at 400 K for 2 h and measured under vacuum conditions; third, the very high quality of our experimental data allows us (as far as the high-Ti-content samples are concerned) to look for preferential framework T sites for Ti substitution, as recently proposed by two different groups on the basis of the results of molecular dynamics modeling (23, 25).

The first aim has great relevance, since it confirms the validity of an absolute method (16) that can be used in any laboratory to check the fraction of Ti incorporated into the TS-1 framework and thus the quality of the synthesis. The second aim extends the applicability of Perego's method to virgin TS-1 samples. This is far from trivial, since pretreatment with  $\text{CH}_3\text{COONH}_4$  strongly modifies both the long-range and local characteristics of the material. This has been evidenced by (i) a systematic increment in cell volume of  $\approx 15\text{--}18 \text{ \AA}^3$  (see below) and (ii) a reduction in the density of internal hydroxyl groups as monitored by the decrease in the corresponding O–H stretching band observed by IR spectroscopy (see below) and by the decrease in the amount of irreversibly adsorbed  $\text{NH}_3$  molecules measured by microcalorimetric experiments (26, 27). Finally, the third aim represents (to the best of our knowledge) the first attempt to single out Ti preferential substituting sites in TS-1 from experimental data. The results of our research are important, even if no clear evidence of any preferential substituting site has been recognized; in fact, our results can contribute to the animated theoretical debate among supporters for both the absence (19, 21, 24) and presence (23, 25) of preferential substitution sites.

## 2. EXPERIMENTAL

TS-1 samples with Ti loading ( $x = [\text{Ti}] / ([\text{Ti}] + [\text{Si}])$ ) in the range 0–0.022 were synthesized following Ref. (1) and are

summarized in Table 1. All samples were calcined at 823 K; those marked with asterisks were treated with aqueous ammonium acetate solution and further calcined following Ref. (16). The latter samples are referred to as “treated” samples hereafter.

Both treated and untreated TS-1 samples activated under dynamic vacuum at 400 K for 2 h were transferred (*in vacuo*) into a borosilicate glass capillary for XRPD measurements. The 1-mm-diameter capillaries were sealed and mounted on the sample spinner on the  $\omega$  axis of the diffractometer, to optimize the statistical orientation of the powder crystallites and minimize preferred orientation effects.

Powder diffraction patterns (28) were collected at powder diffraction beam line BM16 (29) of the ESRF, Grenoble, at a wavelength of  $\lambda = 0.85018(1) \text{ \AA}$ . The experimental setup was similar to that used previously for the study of Na–Rb–Y zeolite (30). The wavelength was calibrated with NIST Si Standard 640b. The detector bank was scanned from  $2^\circ$  to  $65^\circ 2\theta$  at a rate that varied from  $0.5^\circ/\text{min}$  at low angle to  $0.1^\circ/\text{min}$  at high angle. Diffraction patterns were collected in a continuous scanning mode, for a little over 6 h, with the high-angle regions being scanned more than once to improve the statistical quality of the patterns. Following data collection, the data from the nine counters were summed as described previously (30).

Rietveld refinement (31) was performed in space groups  $Pnma$  and  $P2_1/n11$  (for the orthorhombic and monoclinic samples, respectively) using the program GSAS (32) over the angular range  $6^\circ\text{--}60^\circ 2\theta$  ( $0.85 \leq d \leq 8.12 \text{ \AA}$ ), with a pseudo-Voigt peak-shape function modified for asymmetry with four refinable coefficients. The background was treated using a Chebishev polynomial of the first kind with 12 refinable coefficients. An overall scale factor, the cell parameters, and the zero angle shift were also included. Starting atomic coordinates for the two samples were taken from Refs. (33) and (34) (monoclinic and orthorhombic, respectively). Because of the complexity of the structural model, restraints on (Si/Ti)–O and O–O distances were applied.

Their weight was progressively reduced in the final cycles. A single isotropic displacement parameter was imposed for all T sites and for all oxygen atoms. All refinements satisfactorily converged to profile agreement factors in the range  $5.67 < R_{wp} < 11.88$  and to structure agreement factors in the range  $0.05 < R_{F^2} < 0.09$ .

The typical high quality of the measured synchrotron XRPD patterns and the good fit of the refined models can be appreciated in Fig. 2 for sample /13\*. The refined positions of Si and O atoms for this sample are listed in Table 2. For all the other TS-1 samples studied the  $R_{wp}$  and  $R_p$  parameters are reported in Table 1 together with the FWHM value at  $2\theta = 12.6342^\circ$ .

No significant density was detected in the difference Fourier maps. The presence of Ti on T sites was tested using different refinement strategies (see Section 3.2 for details) and the results are summarized in Table 3.

IR measurements were performed at room temperature. Thin self-supporting wafers of TS-1 were prepared and activated *in vacuo* at 400 K for 2 h, inside an IR cell which allowed *in situ* high-temperature treatments and low-temperature measurements to be made. The IR spectra

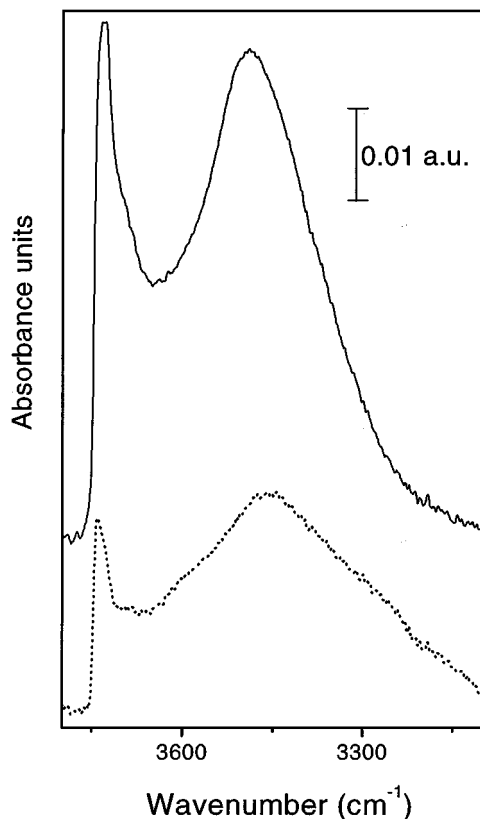


FIG. 1. IR spectra in the O-H stretching region of sample /1 before (solid line) and after (dotted line) treatment with ammonium acetate and successive calcination. The former spectrum has been vertically shifted for graphic reasons.

TABLE 2

Atomic Parameters Resulting from the Rietveld Refinement of Orthorhombic TS-1 Sample ( $x = 0.0201$ ) Treated with Ammonium Acetate<sup>a</sup>

Atom	$x$	$y$	$z$	$U_{iso}$ (Å <sup>2</sup> )
Si1	0.4233(6)	0.0576(8)	-0.3342(9)	0.0103(5)
Si2	0.3109(8)	0.0293(6)	-0.1846(9)	0.0103(5)
Si3	0.2783(6)	0.0627(7)	0.0343(9)	0.0103(5)
Si4	0.1186(6)	0.0620(8)	0.0316(9)	0.0103(5)
Si5	0.0716(6)	0.0271(7)	-0.182(1)	0.0103(5)
Si6	0.1905(7)	0.0585(7)	-0.3276(8)	0.0103(5)
Si7	0.4244(7)	-0.1727(6)	-0.324(1)	0.0103(5)
Si8	0.3106(8)	-0.1281(6)	-0.1799(9)	0.0103(5)
Si9	0.2749(6)	-0.1732(6)	0.0333(9)	0.0103(5)
Si10	0.1194(7)	-0.1739(6)	0.035(1)	0.0103(5)
Si11	0.0730(7)	-0.1299(7)	-0.180(1)	0.0103(5)
Si12	0.1891(8)	-0.1747(5)	-0.3125(8)	0.0103(5)
O1	0.3756(9)	0.061(1)	-0.238(1)	0.020(1)
O2	0.305(1)	0.0614(9)	-0.077(1)	0.020(1)
O3	0.1991(6)	0.063(1)	0.028(1)	0.020(1)
O4	0.0942(9)	0.0593(1)	-0.080(1)	0.020(1)
O5	0.1195(8)	0.051(1)	-0.271(1)	0.020(1)
O6	0.2479(9)	0.051(1)	-0.249(1)	0.020(1)
O7	0.377(1)	-0.159(1)	-0.230(1)	0.020(1)
O8	0.310(1)	-0.159(1)	-0.070(1)	0.020(1)
O9	0.1965(7)	-0.1516(8)	0.025(1)	0.020(1)
O10	0.088(1)	-0.160(1)	-0.075(1)	0.020(1)
O11	0.1194(9)	-0.160(1)	-0.264(1)	0.020(1)
O12	0.246(1)	-0.155(1)	-0.234(1)	0.020(1)
O13	0.313(1)	-0.0498(6)	-0.177(1)	0.020(1)
O14	0.0808(9)	-0.0512(7)	-0.171(1)	0.020(1)
O15	0.418(1)	0.1304(8)	-0.385(1)	0.020(1)
O16	0.402(1)	0.0004(9)	-0.406(1)	0.020(1)
O17	0.401(1)	-0.1322(9)	-0.420(1)	0.020(1)
O18	0.193(1)	0.1302(8)	-0.381(1)	0.020(1)
O19	0.198(1)	0.0006(9)	-0.406(1)	0.020(1)
O20	0.198(1)	-0.1312(8)	-0.413(1)	0.020(1)
O21	-0.0033(7)	0.045(1)	-0.208(1)	0.020(1)
O22	-0.0025(7)	-0.147(1)	-0.212(1)	0.020(1)
O23	0.428(1)	-0.250000	-0.350(2)	0.020(1)
O24	0.199(2)	-0.250000	-0.345(2)	0.020(1)
O25	0.278(1)	-0.250000	0.062(2)	0.020(1)
O26	0.110(1)	-0.250000	0.064(2)	0.020(1)

<sup>a</sup>Values of  $R_{wp}$  and  $R_p$  parameters are 10.05 and 7.41%, respectively, and  $\chi^2 = 1.522$  for 130 variables. The refined cell parameters are  $a = 20.1468(8)$  Å,  $b = 19.9565(8)$  Å,  $c = 13.4242(5)$  Å [ $V = 5397.3(6)$  Å<sup>3</sup>].

were recorded in transmission mode on a Bruker FTIR88 spectrometer equipped with an MCT cryodetector.

### 3. RESULTS AND DISCUSSION

#### 3.1. Cell Parameters versus Ti Content

In a fundamental work (16), Perego's group showed that in well-manufactured TS-1 samples treated with  $\text{CH}_3\text{COONH}_4$  before recalcination, the cell parameters and, consequently, the unit cell volume increase linearly with the Ti loading of the sample (16). Our results represent

TABLE 3

Ti Partitioning as Obtained by Rietveld Refinement of the Individual Tetrahedral Site Occupancies in the Orthorhombic High-Ti-Content MFI Samples<sup>a</sup>

Sample	T1	T2	T4	T5	T6	T8	T11	T12
/13* (a)	-0.14(3)	-0.08(3)	0.05(3)	0.04(3)	0.00(2)	-0.07(3)	-0.05(3)	0.00(3)
/13* (b)	0.00(2)	0.00(2)	0.08(1)	0.07(1)	0.05(1)	0.00(2)	0.00(2)	0.04(2)
/13* (c)	-0.04(2)	-0.01(2)	0.07(2)	0.06(2)	0.04(2)	-0.04(2)	0.00(2)	0.05(2)
/13 (a)	0.00(2)	0.03(2)	0.25(2)	0.10(2)	—	0.08(2)	0.24(2)	0.10(1)
/16* (a)	0.00(2)	-0.07(2)	0.07(2)	0.12(2)	—	-0.10(2)	—	0.02(2)
/33* (a)	0.00(2)	-0.01(2)	0.02(2)	—	—	—	—	—
/57* (a)	0.05(2)	-0.01(2)	0.11(2)	—	—	-0.05(2)	0.18(3)	0.10(2)
/44 (a)	0.00(2)	0.02(1)	0.02(1)	—	—	—	0.09(2)	—

<sup>a</sup> See Table 1. Only the sites showing a positive amount of Ti in the first refinement step are listed, besides T2 and T8 which were used as test sites in all samples. For sample /13\*, the results obtained using three different refinement strategies, labeled (a), (b), and (c), are reported (see text for details).

a relevant improvement of that important work from three major points of view.

i. Use of a more intense synchrotron radiation source implies an intrinsic enhancement of the signal/noise ratio of our XRPD patterns, allowing full Rietveld refinements up to a  $d$  spacing of 0.85 Å to be performed. This is also due to the optimal instrument contribution to the peak width (approximately  $0.006^\circ 2\theta$  in the low-angle range). The quality of the experimental data and of the corresponding refined X-ray patterns can be appreciated in Fig. 2 for sample /13\*; similar high-quality data were obtained for all samples. To allow a thorough inspection of the high  $2\theta$  data, the experimental pattern was divided into three angular regions for low, medium, and high  $2\theta$  values (a, b, and c, respectively).

ii. The present measurements were performed on dehydrated samples: this eliminates the possible influence of adsorbed molecules on the measured TS-1 cell parameters, allowing us to discard any arbitrary effect related to the history of the sample.

iii. We report, for the first time, a highly linear correlation of  $a$ ,  $b$ ,  $c$ , and  $V$  versus  $x$  on TS-1 samples not previously pretreated with ammonium acetate.

Regarding the last two critical points, Millini *et al.* (16) recommend ammonium acetate treatment of samples measured in air to limit the dispersion of the point in the ( $x$ ,  $V$ ) plane. The effect of the treatment has been rationalized in terms of the relaxation of framework tensions and the cleaning of sample-related effects involving extraframework species. Figure 3 reports the refined cell volumes and cell parameters of treated TS-1 samples as a function of Ti loading (see Table 4 for quantitative data). All samples were previously treated with ammonium acetate following (16). The linearity of the data is in agreement with the cited results, although there is a systematic cell volume increment of about 11–14 Å<sup>3</sup> in the dehydrated samples with respect to the hydrated ones. This implies a strong interac-

tion between the adsorbed water molecules and the TS-1 framework. It is indeed not surprising, considering the effects between the polar water molecule and the Brønsted sites of internal silanol and titanol groups. This is in agreement with a previous IR study in which hydrogen bond interactions of medium and high strength were evidenced by observing the perturbation of the O–H stretching mode of silanols and titanols on interaction with H<sub>2</sub>O (8, 35–39). The same holds for the important direct interaction between water molecules and framework Ti species, as documented by several techniques (UV-vis, IR, EXAFS, XANES) (7–14).

The cell data measured on TS-1 samples not treated with ammonium acetate are shown in Fig. 4, while quantitative data are reported in Table 4. The even higher linear

TABLE 4

Linear Regression Coefficients of Unit Cell Parameters:  
 $Y = mx + q$ , where  $Y = a, b, c$ , and  $V^a$

	$m$	$q$	$r$
Dehydrated, treated TS-1 (present study)			
$a$	1.824 Å	20.106 Å	0.97631
$b$	3.521 Å	19.885 Å	0.99992
$c$	2.093 Å	13.382 Å	0.99886
$V$	2287.5 Å <sup>3</sup>	5350.4 Å <sup>3</sup>	0.99887
Dehydrated, untreated TS-1 (present study)			
$a$	2.410 Å	20.069 Å	0.99945
$b$	2.661 Å	19.880 Å	0.9977
$c$	1.896 Å	13.372 Å	0.9986
$V$	2093.0 Å <sup>3</sup>	5335.8 Å <sup>3</sup>	0.99994
Hydrated, treated TS-1 [Ref. (16)]			
$a$	1.429 Å	20.098 Å	0.9868
$b$	2.975 Å	19.882 Å	0.9924
$c$	2.281 Å	13.363 Å	0.9957
$V$	2110.4 Å <sup>3</sup>	5339.4 Å <sup>3</sup>	0.9993

<sup>a</sup>  $r$  is the correlation coefficient of the linear fit.

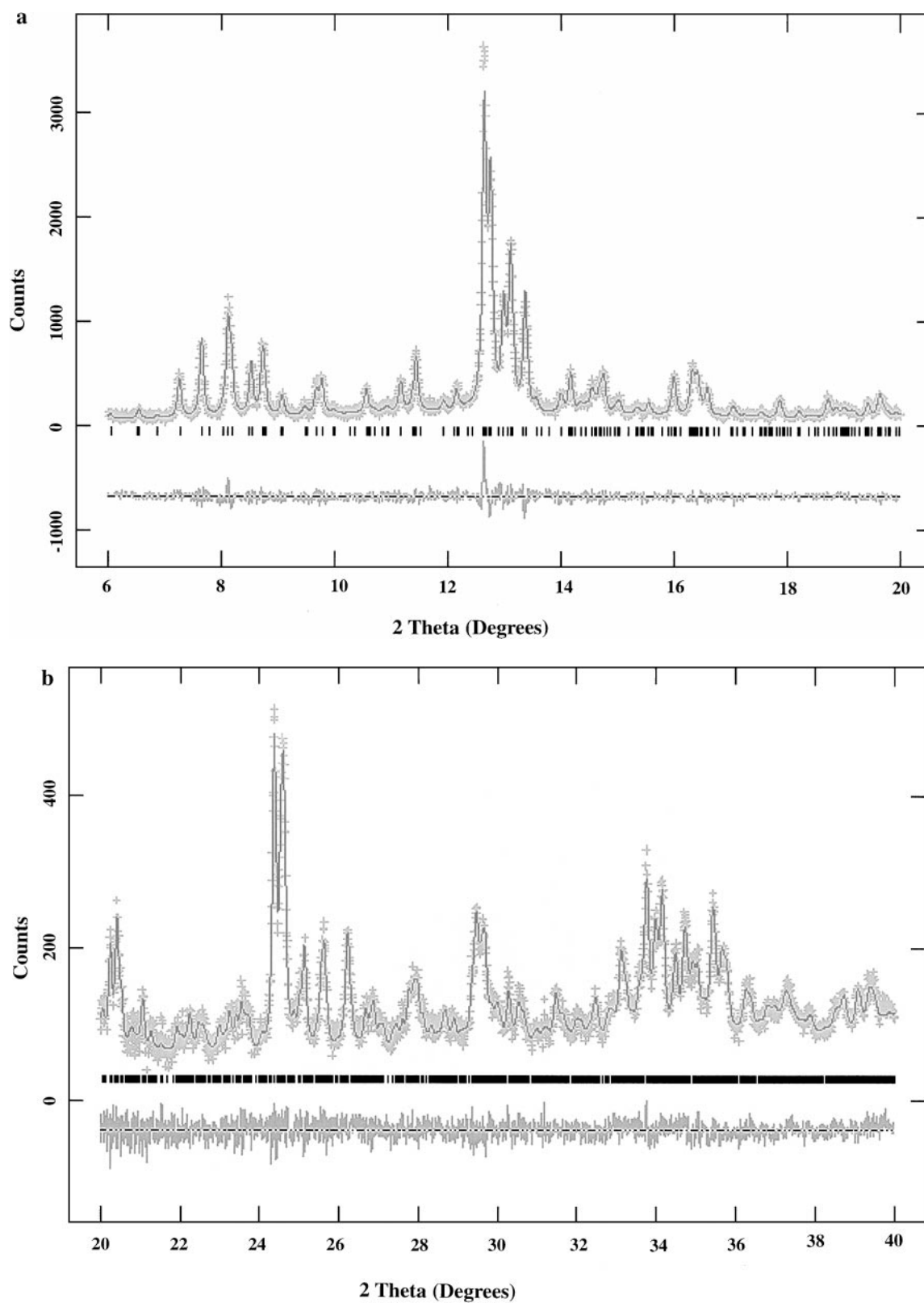


FIG. 2. Observed, calculated, and difference profiles and reflection positions, in the  $2\theta$  regions (a)  $6^\circ$ – $20^\circ$ , (b)  $20^\circ$ – $40^\circ$ , and (c)  $40^\circ$ – $60^\circ$ . These data are referred to sample /13\*; the quality of the refinement for all other investigated samples is equivalent.

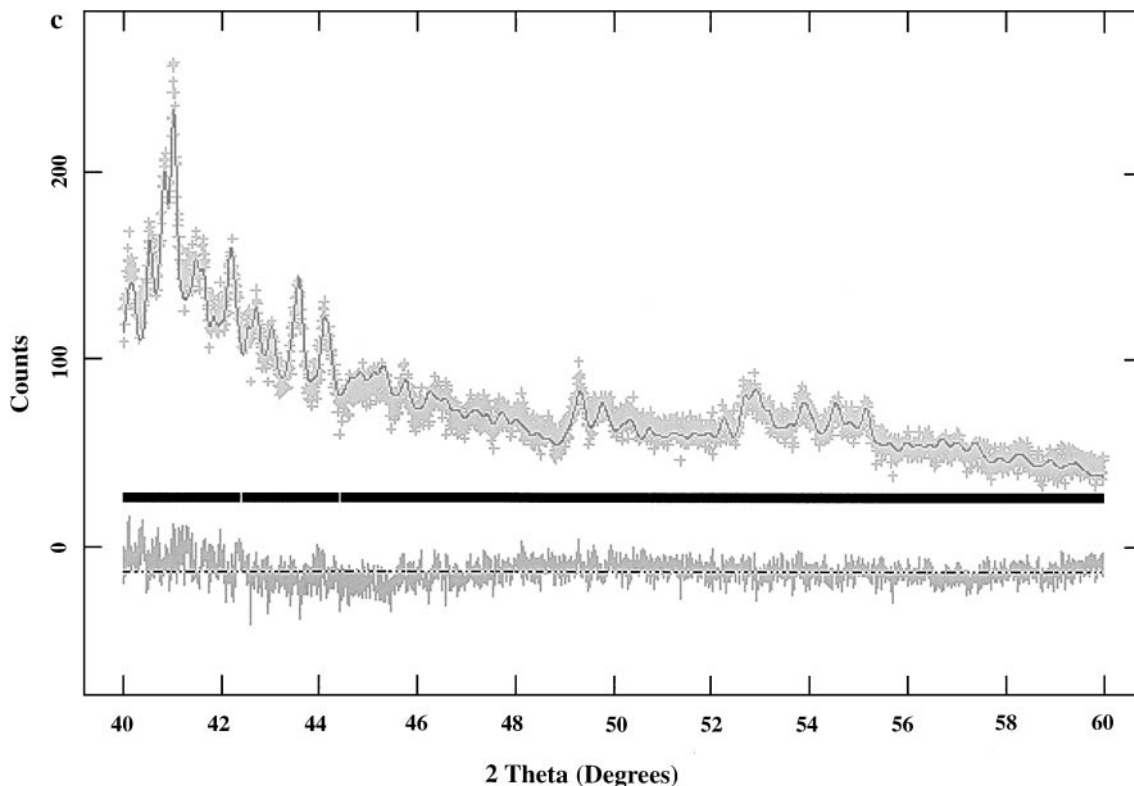


FIG. 2—Continued

correlation between Ti content and cell parameters in these samples (see Table 4) proves that the dehydration procedure also has a positive effect on the dispersion of points in the  $(x, V)$  plane, as reported in the case of sample treatment with ammonium acetate (16).

Detailed comparison between treated and untreated samples shows the following differences:

i. Treated samples show a systematic increment in cell volume of about  $15\text{--}18 \text{ \AA}^3$  (see Table 1), the angular coefficients of the linear fits reported in Figs. 3 and 4 not being seriously affected by the treatment (about 8%, see Table 4).

ii. In the samples with low Ti content (including silicalite) the treatment induces the orthorhombic-to-monoclinic solid-state phase transformation (see the reported value for the  $\alpha$  angle in Table 1).

iii. The treated samples exhibit a minor content of internal point defects, as documented by the intensity reduction of the O–H band in the region  $3800\text{--}3100 \text{ cm}^{-1}$  (Fig. 1). A strong local rearrangement of internal silanol and titanol groups is hypothesized on the basis of the consistent reduction of silanol and titanol groups on treatment with  $\text{CH}_3\text{COONH}_4$ . The IR data reported here are quantitatively confirmed by microcalorimetric experiments of adsorbed  $\text{NH}_3$ , where a decrease in the amount of irreversibly adsorbed  $\text{NH}_3$  molecules has been observed for treated samples (26, 27). It is, however, worth emphasizing that

the treatment with ammonium acetate does not affect the amount of reversibly adsorbed ammonia, which has been measured to be between 1.5 and 2.0 molecules per framework Ti site at  $P(\text{NH}_3) = 50$  Torr. This quantitative value, also confirmed by a parallel EXAFS study and measured for both treated and untreated samples, is independent of the total amount of incorporated Ti, [see Refs. (26, 27) for low- and high-Ti-content samples, respectively].

Considering points i, ii, and iii, it is evident that treatment with  $\text{CH}_3\text{COONH}_4$  has nonnegligible consequences on both the local and long-range structures of TS-1. This means that the empirical recommendation given in Ref. (16) to reduce the dispersion of the points in the  $(x, V)$  plane has the parallel effect of perturbing the material. Now, given the observed high linear correlation also found for the untreated samples measured under carefully dehydrated conditions (Fig. 4 and Table 4), it has been proven that dehydration represents a serious alternative to treatment with ammonium acetate in measuring the total amount of Ti incorporated into TS-1 by XRPD. This methodology allows us to discard any arbitrary effect related to the history of the sample, avoiding any strong perturbations in it. Of course, as XRPD in a controlled atmosphere is a rather complicated technique, the empirical pretreatment with ammonium acetate remains strongly recommended for samples measured under normal conditions.

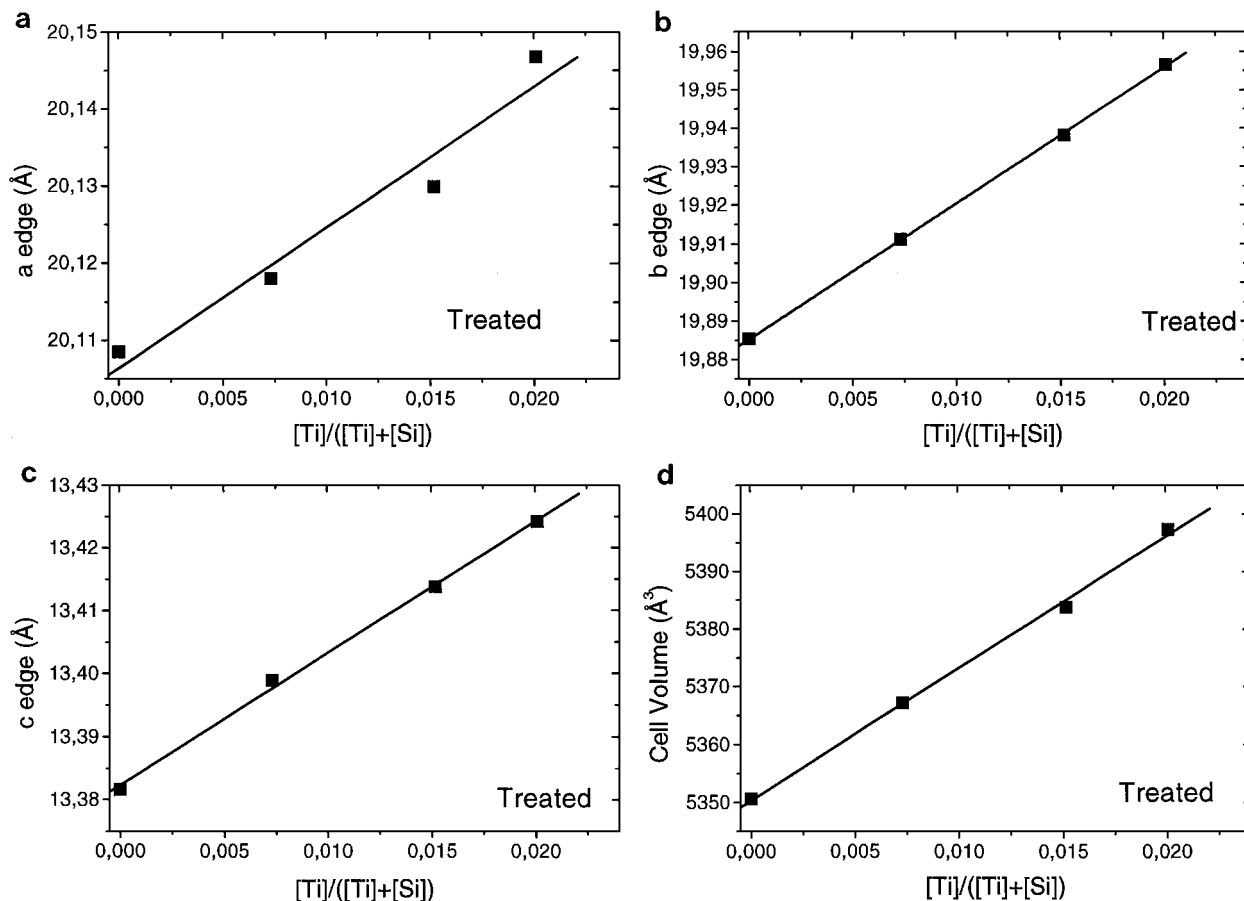


FIG. 3. Refined cell parameters (a)  $a$ , (b)  $b$ , and (c)  $c$  and (d) cell volume  $V$  versus Ti content  $x$  for TS-1 samples treated with ammonium acetate.  $x = [\text{Ti}]/([\text{Ti}] + [\text{Si}])$ .

### 3.2. About Preferential Substitution Sites

In the Introduction we rapidly reviewed the most relevant structural and spectroscopic results unambiguously proving the isomorphous substitution of Ti atoms in the MFI tetrahedral framework. The possible presence of preferential substitutional T sites is now open to discussion. The very low Ti content [ $x \leq 0.025$  (16)] of the samples makes any direct attempt to define the Ti sites using spectroscopic techniques or XRPD with conventional X-ray sources impossible. To date, the most interesting results concerning Ti partitioning are derived from computational chemistry (19, 21, 23–25).

The first theoretical contribution to the debate (19) used defect energy minimization and quantum mechanical cluster computation to study the isomorphous Ti substitution in monoclinic MFI. Jentys and Catlow reported that Ti substitution is energetically favored (about  $21 \text{ kJ mol}^{-1}$ ) and leads to Ti atoms tetrahedrally bonded to four framework oxygens at a distance of  $1.78 \text{ \AA}$ . The distances obtained are very close to those experimentally found by EXAFS experiments on well-manufactured TS-1 samples, where Ti–O dis-

tances in the range  $1.79$ – $1.81 \text{ \AA}$  were reported (11, 12, 15, 17, 18). The results in Ref. (19) are also in full agreement with UV–vis and XANES evidence. The presence of extraframework Ti-containing clusters proposed in the literature was discarded because no stable Ti position was found in such configurations. Moreover, Jentys and Catlow (19) concluded that among the 24 different T sites of the monoclinic MFI unit cell, no clear energetic preference emerged from the calculation.

Millini *et al.* (21), who performed local density functional quantum mechanical calculations on pentameric  $\text{Ti}(\text{OSiO}_3\text{H}_3)_4$  clusters to investigate isomorphous Ti substitution in the orthorhombic MFI framework, came to the same conclusions. They used a fixed cluster geometry, closely conforming to the geometry of the MFI framework (21). The Ti–O distance ( $1.80 \text{ \AA}$ ) obtained was in full agreement with experimental data. By substituting Ti in the 12 different T sites of the orthorhombic cell they found a relatively small spread of energy and concluded in favor of a homogeneous distribution of the heteroatoms.

On the contrary, Oumi *et al.* (23) investigated the isomorphous substitution of Ti in the orthorhombic MFI framework

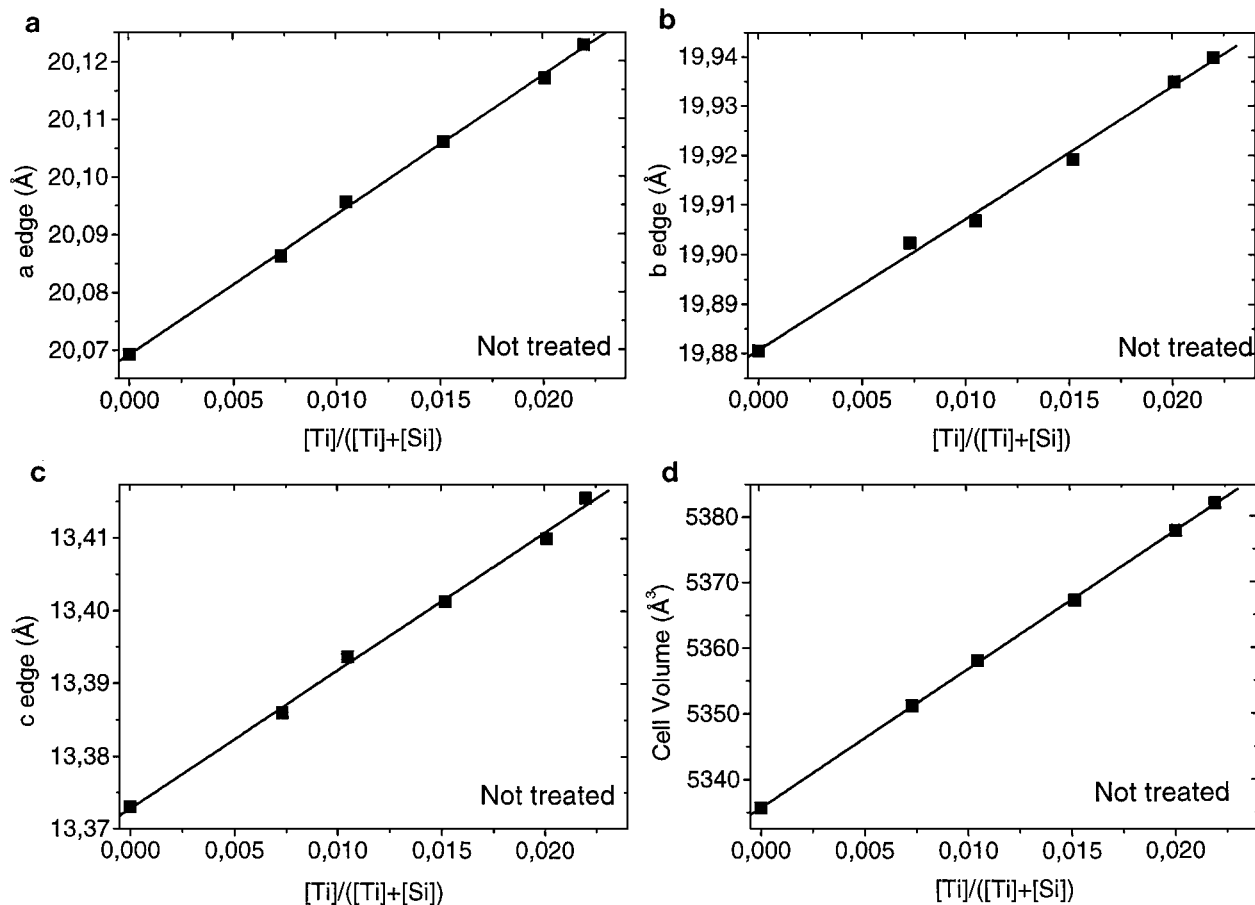


FIG. 4. As in Fig. 2 for TS-1 samples not treated with ammonium acetate.

using a molecular dynamics (MD) approach. The interesting result of their work is the claim that the lattice parameter expansion along the three crystallographic axes is related to the particular substitutional sites. They reported, for the 12 different T sites, the expansion of  $a$ ,  $b$ , and  $c$  assuming that all Ti atoms are incorporated into a single T site and concluded that only substitution into the T8 site is compatible with the experimental  $\Delta a$ ,  $\Delta b$ , and  $\Delta c$  values reported by Perego's group (16). Unfortunately, in a subsequent MD work Smirnov and van de Graaf (24) did not find any correlation between the unit cell expansion and Ti location. It must also be considered that the equilibrium Ti–O distance reported by Oumi *et al.* (23) (1.85 Å) is quite large with respect to the experimental EXAFS values (11, 12, 15, 17, 18).

Lastly, Njo *et al.* (25) reported a study based on combined Metropolis Monte-Carlo and molecular dynamics. Based on previous EXAFS results (11, 12, 15) Njo *et al.* adopted a force field where the Ti–O bond is simulated by a harmonic potential with a minimum at 1.80 Å and a force constant of 211 N/m. The authors (25) arbitrarily located 5 Ti atoms in a double unit cell [effectively approaching the experimental limit of  $x = 0.025$  (16)] and minimized, using a MD

approach, the lattice structure and Ti, Si distribution over 192 T sites (5 Ti and 187 Si). A new T-site distribution was then generated in an inductive way from the previous one by exchanging a Ti with a Si atom, both randomly chosen. The new distribution was subsequently minimized and immediately accepted if its energy ( $E_{i+1}$ ) was lower than that of the previous one ( $E_i$ ). If not, its Boltzman probability  $w = \exp[-(E_{i+1} - E_i)/k_B T]$  was compared with a randomly generated number  $n$ , where  $0 < n < 1$ . If  $w > n$  the new distribution was accepted; otherwise, the system returned to the previous Ti, Si distribution. Beside the energy, each minimization also yielded a new value of angle  $\alpha$  related to the orthorhombic  $\leftrightarrow$  monoclinic transition. Njo *et al.* (25) arbitrarily defined the structure as orthorhombic whenever the minimized  $\alpha$  was in the range  $89.9^\circ$  to  $90.1^\circ$ . As a result, beside the T-site population an  $\alpha$  angle population was also obtained, which looks rather symmetric around  $\alpha = 90.0^\circ$ . Following this approach Njo *et al.* (25) found T2 and T12 as preferential sites for Ti partitioning, while T8 [suggested as preferential site from MD calculation in Ref. (23)] was among the less populated sites. One of the claims of Njo *et al.* (25) is that the orthorhombic  $\leftrightarrow$  monoclinic transition is dependent on the substitution site.



In fact, most of the times that a substitution in T12 was accepted, the minimized cell was orthorhombic, while the monoclinic lattice was preferred for Ti insertion in T2.

Now, it must be emphasized that site T8, suggested as a preferential site from MD calculations in Ref. (23), is among the less populated sites following Ref. (25) and that the lattice expansion  $\Delta a$ ,  $\Delta b$ , and  $\Delta c$  values inferred by MD calculations in Ref. (23) for Ti insertion into sites T2 and T12 [suggested as preferential sites in Ref. (25)] are not compatible with the experimental values reported by Perego's group (16). Although the results of Oumi *et al.* (23) and Njo *et al.* (25) are in obvious contradiction we cannot *a priori* exclude that one of these groups is right.

Can our experimental XRPD data contribute in some way to this controversial and important debate?

The quality of the Rietveld refinement is not improved significantly by introducing the Ti atoms on tetrahedral sites, and furthermore no significant density was detected in the difference Fourier maps. However, an attempt was made to test the preference of Ti atoms for the different tetrahedral sites, employing different refinement strategies. The different approaches were first tested and critically compared on sample /13\*, as it is one of the samples showing the highest Ti content. Successively the selected strategy was applied to all samples having a high Ti content (i.e., /13\*, /13, /16\*, /33\*, /57\*, /44; Table 1).

The refinement strategies tested on sample /13\* are as follows: (a) simultaneous refinement of the Ti and Si proportion ( $Ti + Si = 1.0$ ) in all tetrahedral sites, with no limitation on overall Ti content; (b) simultaneous refinement of the Ti and Si proportion ( $Ti + Si = 1.0$ ) in all tetrahedral sites, with the total Ti content of the sample constrained to the value measured by chemical analysis (i.e., 1.93 Ti atoms per cell; Table 1); and (c) refinement of the Ti and Si content ( $Ti + Si = 1.0$ ) of individual T sites one at the time, with no chemical constraints. The site occupancy factors resulting from the different refinements for sample /13\* are listed in the first three rows of Table 3. In all cases a unique isotropic displacement parameter factor ( $U_{iso}$ ) was used for the 12 T sites to limit the number of refined parameters.

The tests performed on sample /13\* clearly indicate that the refinement strategy does not substantially influence the final results. The T sites containing significant amounts of Ti are independent of the refinement assumptions: sample /13\* always shows appreciable Ti occupancy only in sites T4, T5, T6, and T12, although the total absolute Ti content is slightly influenced by the overall chemical constraints.

We therefore chose to apply the unconstrained refinement strategy (a) to all samples as follows: first the proportion of Ti and Si ( $Ti + Si = 1.0$ ) was allowed to vary simultaneously for each of the 12 tetrahedral sites, using a unique isotropic displacement parameter fixed at the previously refined value. In a second step, the Ti content was reset to 0 and fixed for all the T sites showing a negative Ti content.

The Ti and Si fractional site occupancies were then allowed to vary again for the remaining sites, together with the displacement parameter. The results are reported in Table 3.

Perusal of Table 3 indicates that Ti content above the  $3\sigma$  level is found only in sites T4, T5, T11, and T12. All our attempts to refine part of the site scattering as Ti in sites T2 and T8 [indicated as preferential sites for Ti partitioning by (23, 25)] consistently resulted in full T-site occupancy by Si atoms. The overall results indicate that in several samples there is no clear evidence of Ti partitioning, in agreement with the cited quantum mechanical calculations (19, 21). In a few samples there might be a slight tendency for Ti partitioning, but the preferred T sites vary in different samples.

Furthermore, the results for sample /13, which was measured both before and after treatment with ammonium acetate, show discrepancies larger than expected on the basis of the estimated standard deviations (i.e., sites T4 and T11). Of course we do not expect the treatment to induce Ti exchange between framework T sites, and therefore we take the results as an indication that small residual parameter correlations are always present in the refinements. We can conclude that there is no clear evidence of preferential substitution sites. Finally, it is worth emphasizing that this conclusion is in agreement with recent microcalorimetric data on  $NH_3$  adsorption on TS-1 (27), where the evolution of the heat of adsorption with coverage was found to be typical of heterogeneous surfaces. This experimental evidence has been interpreted in terms of a distribution of Ti in several T sites, favoring the random distribution model. In fact, owing to the high dilution of the titanium centers in TS-1 we expected a homogeneous distribution of the Ti adsorbing sites only in case of a strongly preferential T site (27).

#### 4. CONCLUSIONS

We have presented very high quality XRPD data collected using synchrotron radiation emitted from the bending magnet 16 at the ESRF on a set of dehydrated TS-1 samples with  $x$  values in the range 0–0.022. The cell volume, refined by the Rietveld method, exhibits a highly linear correlation,  $r = 0.99994$ , with  $x$ :  $V(x) = (2093.0 \text{ \AA}^3)x + V(0)$  [ $V(0) = 5335.8 \text{ \AA}^3$ ]. Our work represents an improvement of the important work of Perego's group (16) done on hydrated TS-1 previously treated with ammonium acetate and further calcined. We have proved that when XRPD measurements are performed in a carefully controlled vacuum a highly linear correlation between  $V$  and  $x$  is obtained without the need for sample pretreatment.

Finally, the tests performed on our very high quality powder diffraction data lead us to conclude that the presence of preferential substitution tetrahedral sites for Ti, inferred on the basis of molecular dynamics studies [T8 by Oumi *et al.* (23), T2 and T12 by Njo *et al.* (25)] is very unlikely.

Our experimental results seem to agree with the outcome of the quantum mechanical calculations of Jentys and Catlow (19) and Millini *et al.* (21), namely that Ti is homogeneously distributed on the MFI framework or may be slightly partitioned on different sites in different samples.

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