JOURNAL OF CATALYSIS **151**, 77–86 (1995)

Catalytic Activity of Titanium Silicates Synthesized in the Presence of Alkali Metal and Alkaline Earth Ions

Charles B. Khouw and Mark E. Davis[1]

Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received April 4, 1994; revised September 2, 1994

Titanium containing aluminum-free ZSM-5 (TS-1) synthesized in the presence and absence of alkali metal and alkaline earth ions are investigated as catalysts for the selective oxidation of alkanes and alkenes using aqueous H_2O_2 as oxidant at temperatures below 100°C. Sodium-exchanged TS-1 is not active for alkane oxidations. Similarly, no catalytic activity is observed for TS-1 synthesized in the presence of high concentrations of alkali metal ions (Si/Na <20). For both cases, the catalytic activity can be restored by washing the solid with acid solution prior to catalytic evaluation. Similar results are obtained for TS-1 synthesized in the presence of other alkali metal ions, e.g., Li, K. However, the presence of alkaline earth ions, e.g., Mg, in the synthesis gel does not have a significant effect on the catalytic activity of TS-1. Based on the catalytic data and the physicochemical properties of the samples, a plausible explanation for the above results is described. The acid treatment may be useful in overcoming the problems of synthesizing TS-1 from reagents that contain alkali metal ions, e.g., TPAOH solutions. More importantly, this treatment opens the possibility of synthesizing other titanium-containing silicate structures that require the presence of alkali metal ions in the synthesis gel for their formation. © 1995 Academic Press, Inc.

INTRODUCTION

The hydrothermal synthesis of the titanium-containing derivative of high-silica ZSM-5 (TS-1) was first reported by Taramasso *et al.* (1) in 1983. Subsequent studies on TS-1 have shown that it is an active catalyst for numerous oxidation reactions including aromatic hydroxylations, alkane oxidations and alkene epoxidations using aqueous hydrogen peroxide (40 wt% aqueous H_2O_2 or less) as the oxidant (1–9). All of these reactions are conducted at relatively low temperatures (<100°C) and pressures (~1 atm). Due to the outstanding catalytic activity of this material, TS-1 is being used commercially in Italy for the production of catechol and hydroquinone (6). Additionally, the TS-1 catalyzed conversion of cyclohexanone into cyclohexanone oxime is operating at pilot-plant scale (10).

Several studies have been conducted to understand the nature of the titanium-active site in TS-1. It has been postulated that the catalytic activity on TS-1 is related to the presence of isolated framework titanium species (11). Boccuti *et al.* (12), using UV–VIS spectroscopy, showed that the titanium sites are tetrahedrally coordinated in contrast to the previously proposed titanyl structure [Ti=O] (6). Tuel *et al.* (13) provided further support for tetrahedral coordination by investigating the EPR spectra of Ti^{+3} (obtained by reducing the Ti^{+4} in TS-1 with CO). Additionally, Pei *et al.* (14) show by EXAFS experiments that the titanium sites in TS-1 are tetrahedrally coordinated. EXAFS analyses on the nature of titanium in Ti-Al-β suggest that the coordination number of titanium varies depending upon whether the samples are as-made, calcined, hydrated, or dehydrated (15). Additionally, EXAFS studies carried out by Bonneviot *et al.* (16) support the idea that the Ti^{+4} in TS-1 is tetrahedrally coordinated when the samples are dehydrated and octahedrally coordinated in the presence of water. The XPS data of TS-1 show an identical binding energy to that of Ti(IV) in TiO_2–SiO_2 glasses suggesting that the oxidation state of the titanium in TS-1 is +4 (17, 18).

It has been reported that the presence of alkali metal, even in very small amounts, eliminates the catalytic activity of TS-1 (19). This result severely limits the preparation procedures that can be used to synthesize TS-1 since the reagents must be essentially free of alkali metal cations. This is especially true for the preparation of tetrapropylammonium hydroxide (TPAOH) which is used as the structure-directing agent, since the available commercial products contain alkali metal ions (20). Further study on this phenomenon revealed that the presence of alkali metal ions, e.g., Na^+, K^+, in the synthesis gel can completely eliminate the catalytic activity of TS-1; however, the presence of alkali metal ion in the preformed TS-1 does not have any significant effect on the catalytic activity (21). It has been postulated that alkali metal ions present in the synthesis gel prevent the insertion of titanium into the silicalite framework (19). In this study, we report the effect of alkali metal ions on the synthesis of

---

[1] To whom correspondence should be addressed.

0021-9517/95 $6.00
Copyright © 1995 by Academic Press, Inc.
All rights of reproduction in any form reserved.

TS-1, the subsequent physicochemical properties and the catalytic activity and show that the catalytic activity of TS-1 samples synthesized in the presence of alkali metal ions can be restored by acid treatment.

EXPERIMENTAL

Samples

TS-1 was synthesized following the preparation method reported in the patent literature (1). Tetraethylorthotitanate (TEOT) (Johnson Matthey), tetraethylorthosilicate (TEOS) (Aldrich), tetrapropylammonium hydroxide (TPAOH) (1 *M*, Johnson Matthey) solution, and distilled deionized water were mixed, forming a clear solution with the composition:

$$\mathrm{TEOS:TEOT:TPAOH:H_2O} = 1:0.03:0.4:20.$$

Alkali metal- and alkaline earth-ion-containing TS-1 samples were prepared by adding $NaNO_3$ (Aldrich), KNO_3 (Aldrich), $LiNO_3$ (Aldrich), and $MgNO_3$ (Aldrich) into the clear solution described above. Table 1 shows the amount of salt added into the clear solution. The samples are designated as A–TS–1/*x*, where A is the type of the alkali metal or alkaline earth ions and *x* is the Si/A ratio in the gel. After the addition of the salt, the mixtures become cloudy and the pH of the synthesis mixture decreases slightly, e.g., the pH for TS-1 and Na–TS-1/10 synthesis mixtures are 12.34 and 12.08, respectively. These solutions were then stirred for 2 h, transferred into Teflon-lined autoclaves, and statically heated at 175°C for 7 days. The products were recovered by filtration. Prior to the catalytic reactions, all the materials were calcined in air at 550°C for 8 h.

Sodium-exchanged TS-1 was prepared by stirring 1 g TS-1 (calcined) in 100 ml of 1 *M* NaOH or 1 *M* $NaNO_3$ solution at 25°C for 24 h.

TABLE 1

Gel Composition of Alkali Metal and Alkaline Earth Containing TS-1

Catalyst	Na/Si	K/Si	Li/Si	Mg/Si
Na–TS-1/5	0.200	—	—	—
Na–TS-1/10	0.100	—	—	—
Na–TS-1/13	0.075	—	—	—
Na–TS-1/20	0.050	—	—	—
Na–TS-1/50	0.025	—	—	—
Na–TS-1/100	0.010	—	—	—
K–TS-1/10	—	0.10	—	—
Li–TS-1/10	—	—	0.10	—
Mg–TS-1/10	—	—	—	0.10

The washed TS-1 samples were prepared by stirring the calcined samples in 1 *M* H_2SO_4 (Fisher) for 12 h at room temperature or by stirring in 1 *M* NH_4NO_3 (Aldrich) solution for 12 h at reflux temperature followed by calcination at 550°C for 8 h.

Analysis

X-ray diffraction (XRD) powder patterns were collected on a Scintag XDS-2000 diffractometer that is equipped with a liquid-nitrogen-cooled Germanium solid-state detector and uses CuK_α radiation. Silicon was used as an internal standard for the calculation of unit cell parameters. The XRD data were taken with a step size of 0.02° and a step time of 15 s. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet System 800 Spectrometer (KBr beamsplitter and DTGS detector) using the KBr pellet technique (~2.5 wr% sample). Raman spectra were recorded on the Nicolet Raman accessory for the FTIR system described above (CaF_2 beamsplitter and a liquid-nitrogen-cooled germanium detector). Diffuse reflectance UV (DR–UV) spectra were obtained on a spectrometer system constructed from an EG&G PAR diode array (1024 element Si) detector and a high-radiance Oriel deuterium lamp. The spectra were ratioed to a reference spectrum obtained from powdered MgO. The nitrogen adsorption isotherms were collected at 77 K on an Omnisorp 100 analyzer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Scanning electron micrographs were recorded on a CamScan Series 2-LV SEM.

Catalytic Reactions

The oxidation of *n*-octane (Aldrich) was performed in a 10-ml glass reactor. A typical reaction mixture would contain 20 mg catalyst, 3 mmol *n*-octane, 2.9 mmol H_2O_2 (30% in H_2O, stabilized) (Mallinkrodt), and 0.5 ml methyl ethyl ketone (MEK) (Mallinkrodt) as the solvent. The reactions were conducted at 80°C for 4 or 24 h with vigorous stirring. The epoxidation of 1-hexene (Johnson Mathey) was carried out using 20 mg catalyst, 5 mmol of 1-hexene, 2 mmol of H_2O_2 (30% in H_2O, stabilized), and 3 ml MEK as the solvent. The reaction was conducted at 50°C for 2 h with vigorous stirring in a 10-ml glass reactor immersed in a constant-temperature oil bath.

Prior to analysis, the reaction mixtures were diluted with acetone in order to obtain a single, homogeneous phase. In all cases, mesitylene was used as an internal standard for gas chromatography analysis. The products were analyzed on a HP 5890 Series II GC equipped with a 25-m-long HP-FFAP (polar) capillary column. Hydrogen peroxide conversions were measured by titration with 0.1 *N* $Ce(SO_4)_2$ using ferroin as the indicator. Hydrogen peroxide efficiency was calculated by dividing the amount of

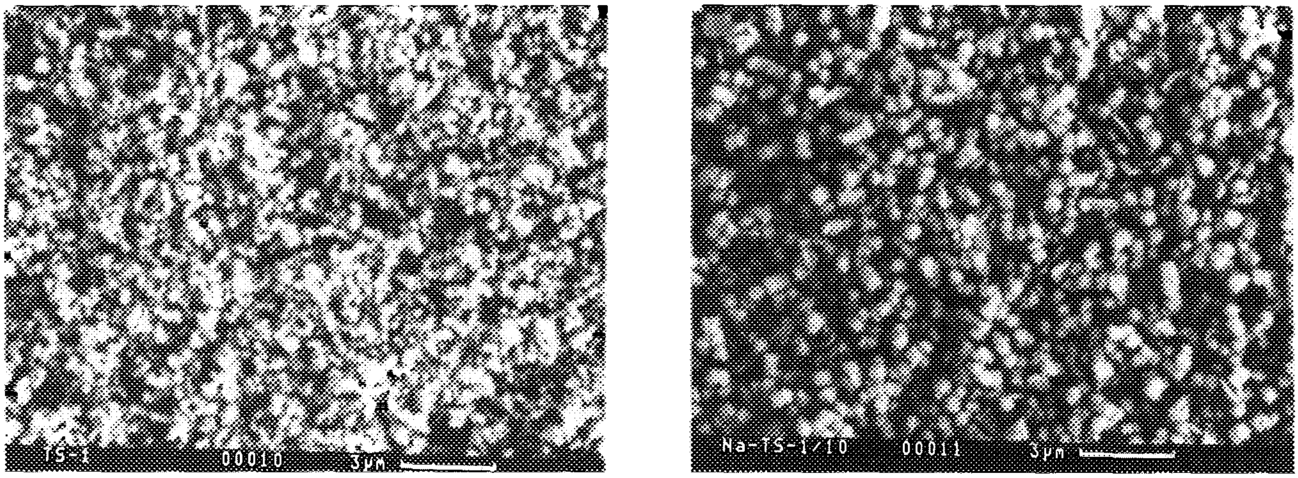


FIG. 1. Scanning electron micrographs of TS-1 and Na–TS-1/10.

H_2O_2 converted to form alcohols and ketones (1 mol of H_2O_2/mol of alcohol formed and 2 mol of H_2O_2/mol of ketone formed) by the amount of H_2O_2 consumed during the reaction.

RESULTS AND DISCUSSIONS

X-ray diffraction patterns reveal that all the materials synthesized here are TS-1 and do not contain additional crystalline phases. (The presence of any extraframework titanium in these materials is not observable by XRD.) The particle size of the materials used in this study ranges from 0.4 μm (TS-1) to 0.8 μm (Na–TS-1/5). The samples synthesized with alkali metal ions tend to be larger than in their absence. Figure 1 shows the scanning electron micrographs of the titanium silicates synthesized in the presence and absence of sodium. The addition of alkali metal ions in the synthesis gel appears to enhance the crystallization rate of TS-1, most likely in a manner described previously for the effect of alkali metal ion the crystallization rate of ZSM-12 (22).

It has been reported that the presence of an IR band at ~960 cm^{-1} is a characteristic of titanium-containing molecular sieves (11). Huybrechts *et al.* (23) have shown that after contacting TS-1 with H_2O_2, the magnitude of this band decreases and eventually disappears. However, by heating the H_2O_2 treated samples at 60°C for 1 h, the original IR spectrum of TS-1 reappears. Several years later, Clerici *et al.* (24) showed that a stable titanium peroxo complex in TS-1 can be synthesized by contacting TS-1 with H_2O_2 in basic medium, e.g., NaOH, KOH. After this treatment, the IR band at ~960 cm^{-1} disappears. Figure 2 shows the IR spectra of TS-1 treated with H_2O_2 and/or base. Contrary to what has been reported earlier, the ~960 cm^{-1} IR band of TS-1 remains un-

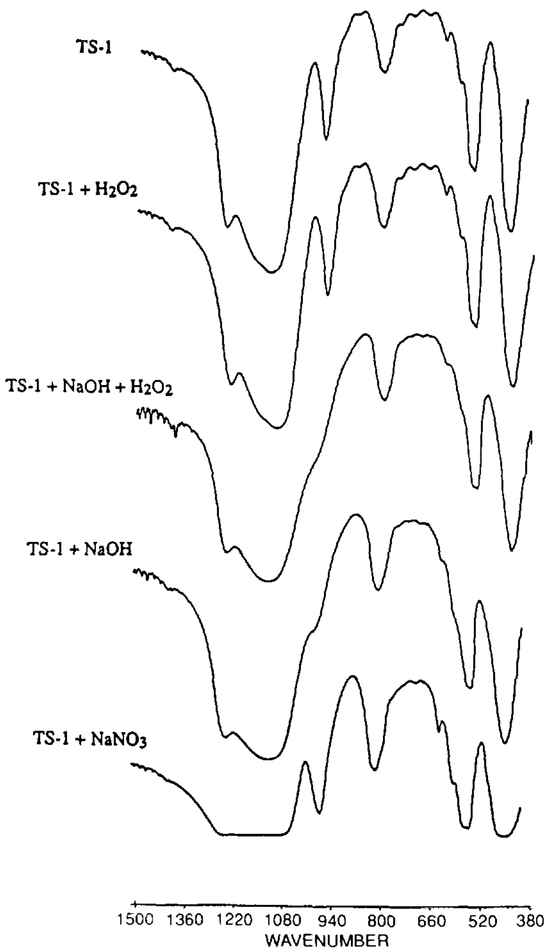


FIG. 2. IR spectra of TS-1 treated with 1 *M* $NaNO_3$, H_2O_2, and/or 1 *M* NaOH solution.

changed when contacted with H_2O_2. Nevertheless, when sodium hydroxide is present in the solution (independent of the presence of H_2O_2), the intensity of IR band at ~960 cm^{-1} decreases and the band is converted into a shoulder at 985 cm^{-1}. The IR band at ~960 cm^{-1} was originally assigned to the stretching vibration of $Si\text{–}O^{\delta-} \cdots Ti^{\delta+}$ (12). However, more recently, Camblor *et al.* (15) reported that this band is better assigned to the stretching vibration of the $Si\text{–}O^-$ groups where H^+, tetraethylammonium$^+$, and/or Na^+ can act as the countercations. This assignment is in agreement with the fact that the IR bands of calcined and uncalcined samples are different and is also consistent with the shifting of the IR band position for Na-exchanged TS-1. Moreover, this result suggests that sodium exchange on TS-1 occurs at the silanol group as illustrated in Scheme 1. Scheme 1 is supported by the fact that a strong base is required in order for the exchange to occur; the ~960-cm^{-1} IR band of TS-1 exchanged with $NaNO_3$ solution remains unchanged and elemental analysis on this material shows that the amount of sodium in the sample is very low.

Further study on the Na-exchanged TS-1 shows that the presence of an IR band at ~960 cm^{-1} can be regenerated by washing the sample with 1 *M* H_2SO_4 solution as shown in Fig. 3. When this material is exchanged again with NaOH solution, the IR band at ~960 cm^{-1} is converted back into a shoulder. If this material is further washed with acid, the IR band at 960 cm^{-1} reappears again (Fig. 3). Similarly, when the Na-exchanged TS-1 is washed with NH_4NO_3, the IR band at ~960 cm^{-1} reappears, although the magnitude is smaller than observed from the sample washed with H_2SO_4. When the NH_4^+-containing sample is calcined, the magnitude of the IR band at ~960 cm^{-1} increases in size similar to that of the unmodified TS-1 (Fig. 4). As a reference, no IR band at ~960 cm^{-1} is observed for pure-silica ZSM-5 washed with 1 *M* H_2SO_4. Elemental analyses of these samples indicate that TS-1 exchanged with 1 *M* solution of NaOH contains a relatively high amount of sodium that can be washed away by treating the sample with a 1 *M* solution

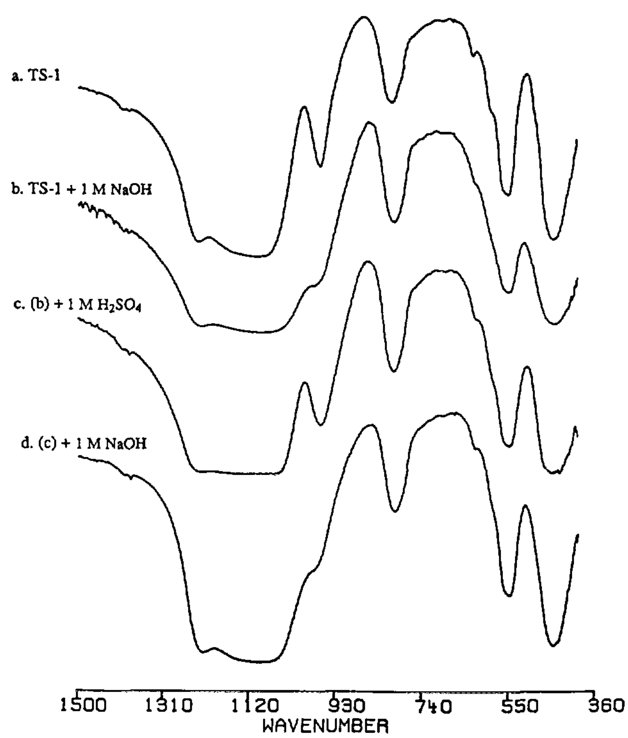


FIG. 3. IR spectra of TS-1 treated with 1 *M* NaOH and/or 1 *M* H_2SO_4 solution.

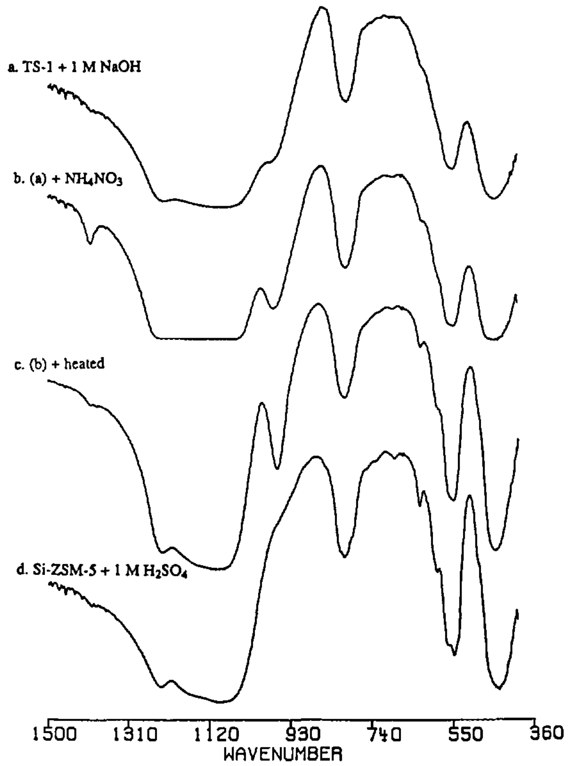
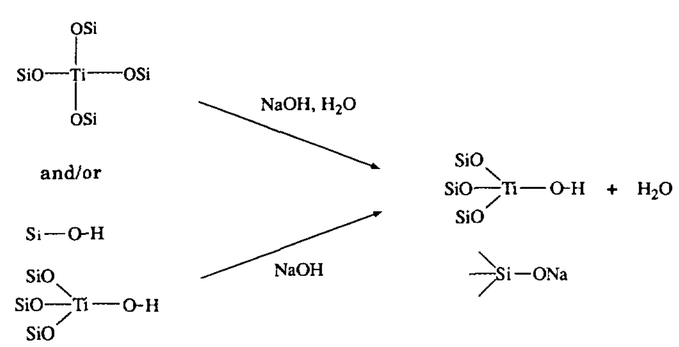


FIG. 4. IR spectra of TS-1 treated with 1 *M* NH_4NO_3 and Si–ZSM-5 treated with 1 *M* H_2SO_4.



SCHEME 1

TABLE 2

Elemental Analyses of TS-1 and TS-1 Treated with Sodium

Catalyst	Si/Ti	Si/Na
(a) TS-1	70	797
(b) TS-1 + $NaNO_3$	n.d[a]	670
(c) TS-1 + NaOH	70	21
(d) (c) + H_2SO_4	81	>1250

[a] n.d., not determined.

TABLE 3

The Effect of Sodium on the IR Band at 960 cm^{-1} and Oxidation of *n*-Octane

Catalyst	IR band (cm^{-1})	Conv. (%)[a]
(a) TS-1	962	20.2
(b) TS-1 + $NaNO_3$	962	18.7
(c) TS-1 + NaOH	985[b]	~1
(d) (c) + H_2SO_4	962	14.2
(e) (d) + NaOH	985[b]	~1
(f) (c) + NH_4NO_3	970	4.8
(g) (f) heated	962	9.4

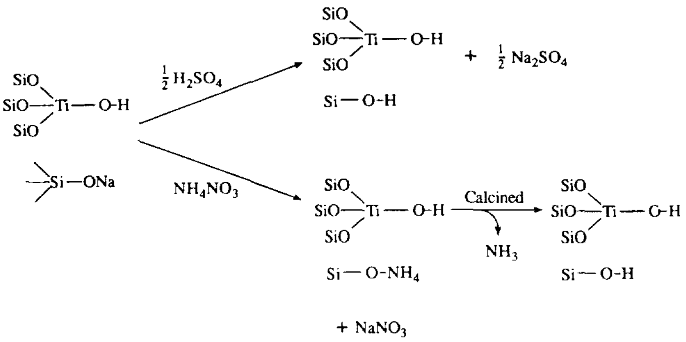
Note. Reaction conditions: 20 mg catalyst, 3 mmol of *n*-octane, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, 80°C, stirred for 24 h in a glass reactor.

[a] Conversion of *n*-octane.

[b] Shoulder.

of H_2SO_4 (Table 2). Additionally, it is also shown that TS-1 exchanged with 1 *M* $NaNO_3$ solution contains only a trace amount of sodium indicating that the exchange only occurs at high pH on TS-1. These observations suggest that Na-exchanged TS-1 can be reversibly converted into its original form by washing it with 1 *M* H_2SO_4 or 1 M NH_4NO_3 (with recalcination) as illustrated in Scheme 2.

Table 3 shows the effect of sodium on the IR band at ~960 cm^{-1} and the catalytic activity of TS-1 for *n*-octane oxidation. TS-1 exchanged with 1 *M* solution of NaOH does not show any catalytic activity for *n*-octane oxidation. However, after washing with 1 *M* H_2SO_4, the catalytic activity of the sample is regenerated (the lack of the complete return of activity may be due to some loss of titanium; see Table 2). Similarly, some of the catalytic activity of Na-exchanged TS-1 is also restored by washing with NH_4NO_3 solution although the activity is lower than the one washed with sulfuric acid solution (even after the sample is heated). This is most likely related to the ion exchange equilibrium between the Na^+ and NH_4^+ ions; not all the sodium in the samples is exchanged by NH_4^+. The correlation between the IR band at ~960 cm^{-1} and the catalytic activity on these materials indicates that only the materials with an IR band at ~960 cm^{-1} are active for *n*-octane oxidation. These observations are in agreement with the previous hypothesis that the IR band at 960 cm^{-1} is a necessary condition for TS-1 to react alkanes (25). Nevertheless, the magnitude of this band does not correlate well with the level of conversion.



SCHEME 2

It has been reported that the presence of alkali metal ions, e.g., Na, in the synthesis gel, even in a very small amount, completely eliminates the catalytic activity of TS-1 (19). Our results on Na-exchanged TS-1 show that it is possible to restore the activity of this material by acid washing. Thus, we explored the possibility of whether acid treatment of TS-1 synthesized in the presence of sodium could restore its catalytic activity. Various amounts of sodium and other alkali metal/alkaline earth ions were introduced into the synthesis gel of TS-1 as indicated in Table 1. The elemental analyses of the sodium containing products are reported in Table 4. As expected, the amount of sodium in the unwashed product decreases as the amount of sodium in the gel is lowered.

TABLE 4

Elemental Analyses of TS-1 Synthesized in the Presence and Absence of Sodium

	Unwashed		Washed w/H_2SO_4 (1.0 *M*)	
Catalyst	Si/Ti	Si/Na	Si/Ti	Si/Na
Na–TS-1/5	28	14	40	553
Na–TS-1/10	26	20	37	>1035
Na–TS-1/13	28	22	39	>924
Na–TS-1/20	36	45	43	>1271
Na–TS-1/50	41	101	42	>670
Na–TS-1/100	50	164	53	>901
TS-1	70	797	76	795

On the other hand, the amount of titanium in the unwashed products remains approximately constant at high concentration of sodium (Si/Na in the gel <20), then decreases as the concentration of sodium in the gel is reduced. After the materials are washed with 1 *M* H_2SO_4, only trace amounts of sodium remain in the samples. The amount of titanium in the washed products also decreases from the amount in the as-synthesized form indicating that some of the titanium is removed by the acid treatment; this is especially true for materials synthesized at a high concentration of sodium in the synthesis gel (Si/Na in the gel <20). It is likely that at high sodium concentration, the titanium inserts into the framework and also forms another compound with sodium; most of this additional compound can be washed away by acid, although some extraframework titanium still remains in the sample (*vide infra*).

The IR spectra of the unwashed materials synthesized in the presence of sodium show a shoulder at 985 cm^{-1} instead of an IR band at ~960 cm^{-1}. However, after these materials are washed with acid, an IR band appears at ~960 cm^{-1} (Fig. 5). Since this band is attributed to the stretching vibration of $Si-O^-$ (12, 15) that is formed due to the incorporation of titanium into the framework, the magnitude of this IR band is also indirectly related to the amount of titanium incorporated into the framework. For the washed Na–TS-1 samples, the magnitude of this band increases as the amount of sodium in the gel decreases. These results indirectly imply that the amount of titanium incorporated into the framework increases as the amount of sodium in the gel decreases.

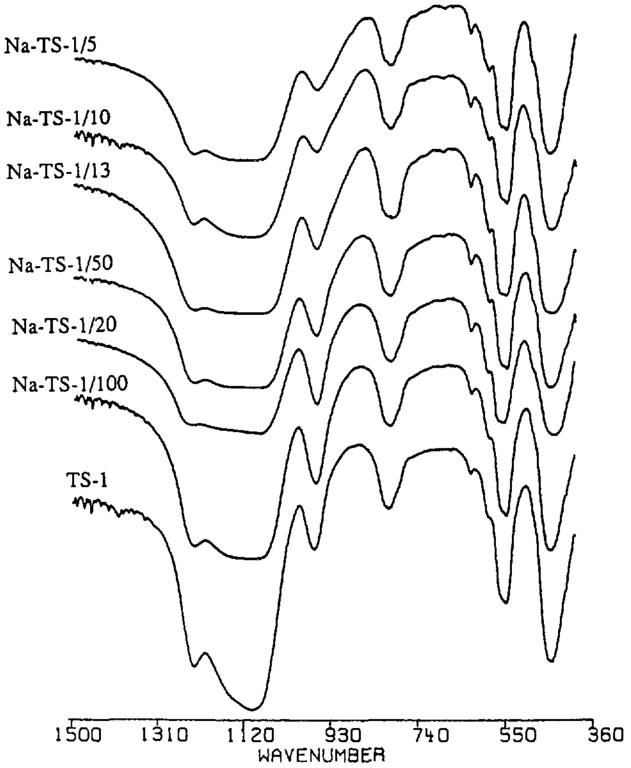


FIG. 5. IR spectra of Na–TS-1 washed with 1 *M* H_2SO_4.

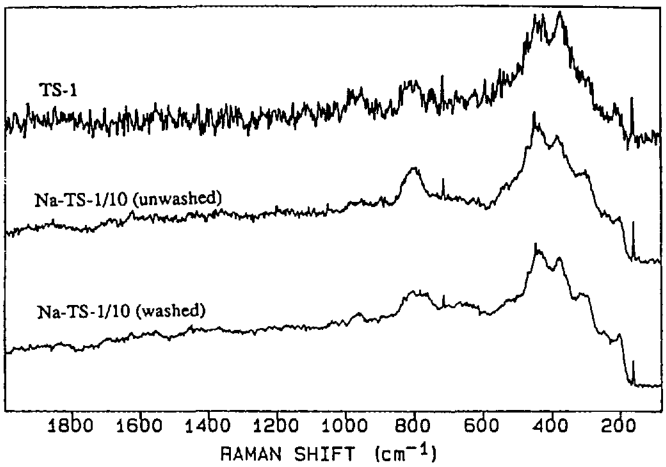


FIG. 6. Raman spectra of TS-1 and Na–TS-1/10.

The Raman spectra of TS-1 and Na–TS-1/10, before and after acid washing, are shown in Fig. 6. The spectra show that no anatase is present. (Anatase peaks occur at 386, 513, and 637 cm^{-1}.) In addition to Raman spectroscopy, ultraviolet diffuse reflectance (DR–UV) spectroscopy has been used to probe the existence of framework and nonframework titanium (12, 23, 26, 27). The DR–UV spectra for the washed Na–TS-1 samples are shown in Fig. 7. The band at 220 nm has been assigned to isolated framework titanium in tetrahedral coordination (12), a broad shoulder around 270 nm has been attributed to the extraframework titanium (28), and the anatase band occurs at 312 nm (29). All of the TS-1 samples synthesized in the presence of sodium show the framework titanium band at 220 nm along with the extraframework band of varying intensities which does not change with acid washing. The amount of extraframework titanium is presumably quite small and is not observed by Raman spectroscopy in the spectral region of greater than 200 cm^{-1}. Based on the DR–UV data, it is evident that only TS-1 synthesized in the absence of sodium is free of extraframework titanium (the spectrum contains only the band at 220 nm indicating all the titanium is in the framework) and the presence of sodium causes the formation of some extraframework titanium. Nitrogen adsorption data from the washed Na–TS-1 samples indicate that no pore blocking due to extraframework titanium and sodium occurs as shown in Fig. 8 for washed Na–TS-1/10. However, the nitrogen adsorption capacity of the washed Na–TS-1 samples are lower than that obtained from "normal" TS-1. This is presumably due to the existence

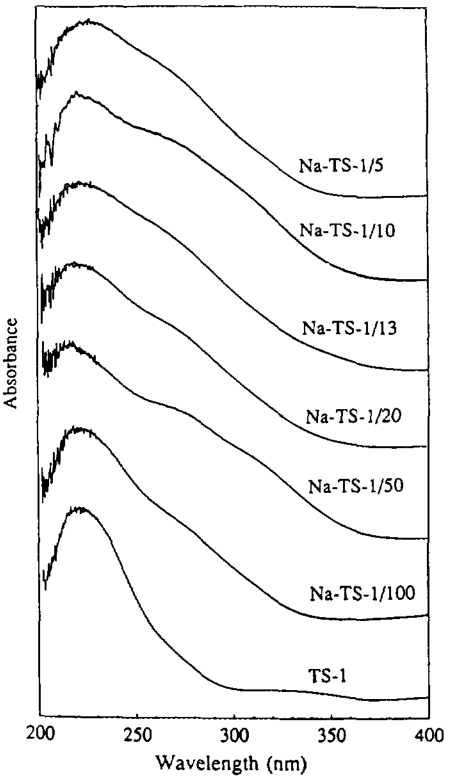


FIG. 7. DR-UV spectra of Na-TS-1 washed with 1 *M* H_2SO_4.

of extraframework materials, e.g., extraframework titanium in these samples that cannot be washed away by the acid treatment.

The catalytic activities of the unwashed materials for the oxidation of *n*-octane are tabulated in Table 5. No activity is observed when the Si/Na ratio in the gel <20.

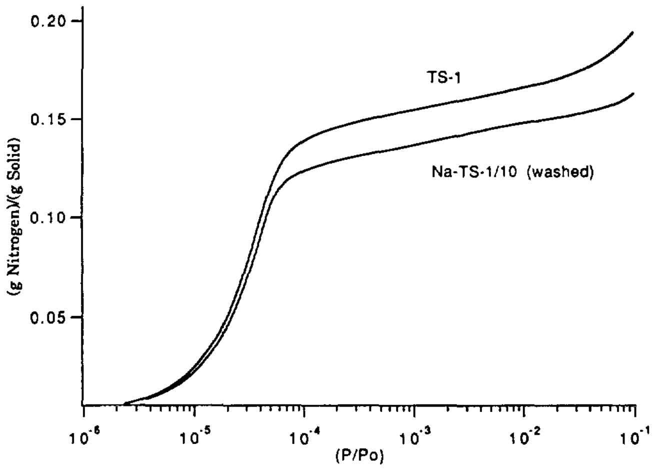


FIG. 8. Nitrogen adsorption of TS-1 and Na-TS-1/10 washed with 1 *M* H_2SO_4.

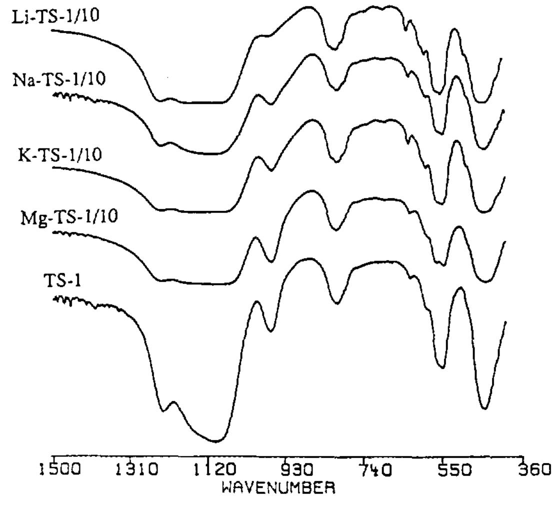


FIG. 9. IR spectra of TS-1 synthesized in the presence of Li, Na, K, and Mg and washed with 1 *M* H_2SO_4.

However, as the concentration of sodium in the gel decreases, the activity increases. Our previous observations on the catalytic activity of Na-exchanged TS-1 suggest that the presence of a Si–ONa group in the neighborhood of the titanium sites inhibits the catalytic activity (30). For TS-1 synthesized in the presence of sodium, we speculate that the sodium in the unwashed samples is in the form of a Si–ONa group that is most likely located in the neighborhood of the titanium sites. Thus, for Na–TS-1 with Na/Ti in the product >1, all the titanium sites are accompanied by the Si–ONa group (similar to the case for Na-exchanged TS-1) so that no catalytic activity should be observed. On the other hand, for Na–TS-1 with Na/Ti <1, not all the titanium sites are accompanied by the Si–ONa group and hence some catalytic activity should be detected. This hypothesis is in agreement with the experimental data (Tables 4 and 5) which indicate that the threshold for the activity occurs at Na/Ti ratio in the products ~1. The H_2O_2 conversions on these materials are close to 100% indicating that sodium containing titanium silicates are very active toward H_2O_2 decomposition.

Table 5 summarizes the catalytic activity of the washed Na–TS-1 samples for alkane activation. All of the washed materials become active and the catalytic activity increases as the concentration of sodium in the synthesis gel decreases. The H_2O_2 conversions from the washed materials are lower than from the corresponding unwashed samples. It is possible that the lack of activity of the unwashed samples is simply because the unwashed materials are more active for H_2O_2 decomposition than for oxidizing the organic substrates.

Surprisingly, the most active material is Na–TS-1/100. Comparison of the IR spectra, elemental analyses and the

TABLE 5

Catalytic Activity of Na–TS-1 for *n*-Octane Oxidation

Catalyst	Unwashed Na–TS-1		Washed Na–TS-1 (w/1.0 *M* H_2SO_4)		
	Conv. (%)[a]	H_2O_2 conv. (%)	Conv. (%)*	H_2O_2 eff. (%)	H_2O_2 conv. (%)
(a) Na–TS-1/5	0	99.5	3.3	8.2	54.0
(b) Na–TS-1/10	0	99.5	7.3	19.8	53.6
(c) Na–TS-1/13	0	98.8	10.9	26.6	53.6
(d) Na–TS-1/20	0.5	98.2	13.7	36.7	61.7
(e) Na–TS-1/50	3.6	99.5	14.8	41.1	58.1
(f) Na–TS-1/100	14.5	99.5	28.0	55.3	91.9
(g) TS-1	16.2	86.5	18.4	41.5	75.2

Note. Reaction conditions: 20 mg catalyst, 3 mmol of *n*-octane, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, 80°C, stirred for 4 h in a glass reactor.

[a] Conversion of *n*-octane.

catalytic data of this sample to those from "normal" TS-1 suggests that more titanium is incorporated into the framework of Na–TS-1/100 although some extraframework titanium may also be present in the sample. Table 6 shows the unit cell parameters calculated from the XRD analysis. Unit cell expansion measurements have been reported to be a very precise method for the evaluation of framework/extraframework Ti (31). It is shown here that the unit cell volume of Na–TS-1/100 is slightly larger than that of TS-1 indicating that a small amount of sodium present in the synthesis gel appears to increase the amount of titanium that can be incorporated into the TS-1 framework. However, as the amount of sodium in the synthesis gel is increased, more extraframework titanium will be formed and less titanium will be incorporated into the framework. Consequently, the catalytic activity of the materials with increasing sodium content will eventually decline. Note that the differences in catalytic activity are not due to the crystal size effect since it has been shown previously that activities observed over the crystal size variation reported here are negligible (32).

Similar to Na–TS-1, the IR spectra of TS-1 synthesized with lithium and potassium do not have a band at ~960 cm^{-1}, instead they show a shoulder at ~985 cm^{-1}. These materials are not active for alkane oxidation. On the other hand, TS-1 synthesized in the presence of magnesium does have an IR band at ~960 cm^{-1} and it is active for *n*-octane oxidation (~8% conversion). The addition of $MgNO_3$ into the synthesis gel results in the precipitation of a white powder. These observations suggest that Mg^{2+} is precipitated as $Mg(OH)_2$ at the basic, synthesis gel condition. Thus, magnesium does not play the same role as alkali metal cations in the synthesis of TS-1. The IR spectra of the TS-1 synthesized with Li, Na, K, and Mg after being washed with acid are shown in Fig. 9. All of these materials contain an IR band at ~960 cm^{-1} which in-

TABLE 6

Unit Cell Data for Titanium Molecular Sieves[a]

Sample	a(Å)	b(Å)	c(Å)	Vol. (Å^3)
Silicalite-1[b]	19.885(4)	20.087(2)	13.374(2)	5341.7
TS-1[b]	19.912(6)	20.096(6)	13.397(7)	5361.2
Na-TS-1/10[c]	19.903(4)	20.084(4)	13.370(5)	5344.7
Na-TS-1/100[c]	19.937(6)	20.111(6)	13.396(7)	5371.5

[a] Orthorhombic symmetry used in all cases.

[b] After calcination.

[c] After calcination and acid treatment.

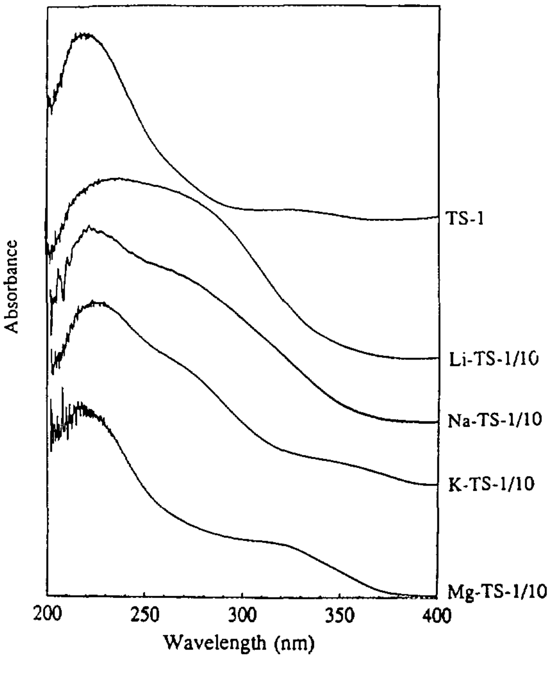


FIG. 10. DR–UV spectra of TS-1 synthesized in the presence of Li, Na, K, and Mg and washed with 1 *M* H_2SO_4.

TABLE 7

Catalytic Activity of TS-1 Synthesized with Various Alkali/Alkaline Earth Washed w/H_2SO_4 (1.0 *M*) for *n*-Octane Oxidation

Catalyst	Si/Ti[a]	Si/Alk[b]	Conv. (%)[c]	H_2O_2 eff. (%)
(a) Li–TS-1/10	44	>567	0.9	7.4
(b) Na–TS-1/10	37	>1035	7.3	19.8
(c) K–TS-1/10	57	>644	9.0	41.9
(d) Mg–TS-1/10	29	56	12.9	24.1

Note. Reaction conditions: 20 mg catalyst, 3 mmol of *n*-octane, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, 80°C, stirred for 4 h in a glass reactor.

[a] Si/Ti ratio in the products.

[b] Si/Alkali metal or alkaline earth ion ratio in the products.

[c] Conversion is based on *n*-octane.

creases in intensity in the following order: Li–TS-1 < Na–TS-1 < K–TS-1 < Mg–TS-1 (may also indirectly imply the incorporation of titanium into the zerolite framework increases in the same order). Figure 10 shows the DR–UV reflectance spectra of these materials. Similar to the spectrum of Na–TS-1, these samples display the framework titanium band at 220 nm along with the band for extraframework titanium. In agreement with the IR data, the DR–UV reflectance spectra also show that the amount of extraframework titanium decreases as the magnitude of the IR band at 960 cm^{-1} increases. The catalytic activity of these materials (Table 7) also increases following the same order as the increase in the IR band intensity at ~960 cm^{-1}. These observations suggest that more titanium is incorporated into the framework as the diameter of the alkali metal ion is increased. The presence of alkaline earth ions in the synthesis gel does not have any significant effect on the catalytic activity of TS-1. However, the material synthesized in the presence of alkaline earth ions contains more anatase than the other samples made with alkali metal ions as shown by the DR–UV broad shoulder at ~310 nm.

As a final test, the catalytic activities of the washed Na–TS-1 samples are examined for 1-hexene epoxidation using aqueous H_2O_2 as the oxidant. The results are listed in Table 8. All the samples are active and the activity increases as the concentration of sodium in the gel decreases. As for *n*-octane oxidation, Na–TS-1/100 is also the most active material in the series for 1-hexene epoxidation.

TABLE 8

Catalytic Activity of Na–TS-1 Washed with H_2SO_4 (1.0 *M*) for 1-Hexene Epoxidation

Catalyst	Conv. (%)[a]	H_2O_2 eff. (%)
(a) Na–TS-1/5	0.5	3.2
(b) Na–TS-1/10	2.6	29.9
(c) Na–TS-1/20	5.4	82.4
(d) Na–TS-1/100	7.4	77.5
(e) TS-1	7.0	64.2

Note. Reaction condition: 25 mg TS-1, 25 mg $MgSO_4$, 5 mmol 1-hexene, 2 mmol H_2O_2 (30% in H_2O), 3 ml MEK, 50°C for 4 h, stirred in a glass reactor.

[a] Conversion of 1-hexene.

CONCLUSIONS

Sodium-exchanged TS-1 is not active for alkane oxidations using aqueous H_2O_2 as oxidant. However, the catalytic activity can be restored by washing the solid with acid solution. Similarly, the catalytic activity of TS-1 synthesized in the presence of sodium can be regenerated by washing with acid. This treatment may be useful in overcoming the problems of synthesizing TS-1 from reagents that contain alkali metal ions, e.g., TPAOH solution. More importantly, this treatment opens the possibility of synthesizing other titanium-containing silicate structures that require the presence of alkali metal ions in the synthesis gel for their formation. We have synthesized titanium-containing SSZ-33 and ZSM-12 and are currently exploring the acid treatment on these materials in order to generate catalytic activity.

ACKNOWLEDGMENT

Support of this work was provided by the Shell Development Co. and the NSF Alan T. Waterman Award to M. E. D.

REFERENCES

1. Taramasso, M., Perego, G., and Notari, B., U. S. Patent 4, 410,501 (1983).
2. Neri, C., Esposito, A., Anfossi, B., and Buonomo, F., Eur. Patent. 100,119 (1984).
3. Neri, C., Anfossi, B., and Buonomo, F., Eur. Patent. 100,118 (1984).
4. Esposito, A., Neri, C., and Buonomo, F., U.S. Patent 4,480,135 (1984).

5. Esposito, A., Taramasso, M., Neri, C., and Buonomo, F., Brit. Patent 2,116,974 (1985).
6. Notari, B., *Stud. Surf. Sci. Catal.* **37,** 413 (1988).
7. Thangaraj, A., Kumar, A., and Ratnasamy, P., *Appl. Catal.* **57,** L1 (1990).
8. Huybrechts, D. R. C., DeBruyker, L., and Jacobs, P. A., *Nature* **345,** 240 (1990).
9. Tatsumi, T., Nakamura, M., Negishi, S., Tominaga, H., *J. Chem. Soc., Chem. Commun.*, 476 (1990).
10. Notari, B., Presented at the 206th National Meeting of the American Chemical Society, Chicago, IL, August 1993; paper PETR 103.
11. Perego, G., Bellussi, G., Cordo, C., Taramasso, M., Buonomo, F., and Esposito, A., *Stud. Surf. Sci. Catal.* **28,** 129 (1986).
12. Boccuti, M. R., Rao, K. M., Zecchina, A., Leofanti, G., and Petrini, G., *Stud. Surf. Sci. Catal.* **48,** 133 (1988).
13. Tuel, A., and Taarit, Y. B., *Appl. Catal.,* **A102,** 69 (1993).
14. Pei, S., Zajac, G. W., Kaduk, J. A., Faber, J., Boyanov, B. I., Duck, D., Fazzini, D., Morrison, T. I., and Yang, D. S., *Catal. Lett.* **21,** 333 (1993).
15. Camblor, M. A., Corma, A., and Pérez-Pariente, J., *J. Chem. Soc., Chem. Commun.,* 1557 (1993).
16. Bonneviot, D. T., On, D. T., and Lopez, A., *J. Chem. Soc., Chem. Commun.,* 685 (1993).
17. On, D. T., and Bonneviot, L., *J. Mol. Catal.* **74,** 233 (1992).
18. Mukhopadhyay, S. M., and Garofalini, S. H., *J. Non-Cryst. Solids* **126,** 202 (1990).
19. Bellussi, G., and Fattore, V., *Stud. Surf. Sci. Catal.* **69,** 79 (1991).
20. Notari, B., *Stud. Surf. Sci. Catal.* **60,** 343 (1991).
21. Khouw, C. B., Li, H. X., Dartt, C. B., and Davis, M. E., in "Catalytic Selective Oxidation" (S. T. Oyama and J. W. Hightower, Eds.), p. 273. ACS, Washington DC., 1993.
22. Goepper, M., Li, H. X., and Davis, M. E., *J. Chem. Soc., Chem. Commun.,* 1665 (1992).
23. Huybrechts, D. R. C., Buskens, P. L., and Jacobs, P. A., *J. Mol. Catal.* **71,** 129 (1992).
24. Clerici, M. G., Ingallina, P., Millini, R., *in* "Proceedings from the Ninth International Zeolite Conference" (R. von Ballmoos, J. B. Higgins, and M. M. J. Treacy, Eds.), p. 445. Butterworth–Heinemann, Boston, 1993.
25. Huybrechts, D. R. C., Vaesen, L., Li, H. X., and Jacobs, P. A., *Catal. Lett.* **8,** 237 (1991).
26. Zecchina, A., Spoto, G., Bordiga, S., Ferrero, A., Petrini, G., Leofanti, G., and Padovan, M., *Stud. Surf. Sci. Catal.* **69,** 251 (1991).
27. Padovan, M., Genoni, F., Leofanti, G., Petrini, G., Trezza, G., and Zecchina, A., *Stud. Surf. Sci. Catal.* **63,** 431 (1991).
28. Kim, Y. L., Riley, R. L., Huq, M. J., Salim, S., Le, A. E., and Mallouk, T. E., *Mat. Res. Soc. Symp. Proc.* **233,** 145 (1991).
29. Clark, R. J. H., "Chemistry of Titanium and Vanadium," p. 272. Elsevier, Amsterdam, 1968.
30. Khouw, C. B., Dartt, C. B., Labinger, J. A., and Davis, M. E., *J. Catal.,* **149,** 195 (1994).
31. Millini, R., Massara, E. P., Perego, G., and Bellussi, G., *J. Catal.* **137,** 497 (1992).
32. Dartt, C. B., Khouw, C. B., Li, H.-X., and Davis, M. E., *Microporous Mater.* **2,** 425 (1994).