

# NMR Spectroscopic Study of the Interaction of 1-Butene with the Titanosilicates TS-1 and ETS-10

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Received July 8, 1994; revised April 22, 1995

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of 1-butene chemisorbed on TS-1 and ETS-10 has been studied. The interaction of butenes with ETS-10 is stronger than with TS-1. ETS-10 is more active than TS-1 for the double-bond isomerization of 1- to 2-butene and both are highly selective. Skeletal isomerization and oligomerization are observed only at high conversion levels. The kinetic rate constants and apparent activation energies have been calculated from changes in the intensity of the NMR lines. Satisfactory agreement is obtained with corresponding values from conventional catalytic reactor data. FTIR spectroscopy reveals the presence of a significant concentration of hydroxyl groups, probably at defect sites, on the surface of both TS-1 and ETS-10. These hydroxyl groups or the Lewis acid sites generated from them on dehydroxylation at high temperatures are probably the active sites in the isomerization reaction. © 1995 Academic Press, Inc.

## INTRODUCTION

TS-1 and ETS-10 are both titanosilicate molecular sieves which differ in their crystal structures. TS-1 has an MFI structure wherein TiO<sub>4</sub> tetrahedra are connected to SiO<sub>4</sub> tetrahedra by corner sharing. The pore system contains 10-membered rings. In ETS-10 (1), corner-sharing SiO<sub>4</sub> tetrahedra and TiO<sub>6</sub> octahedra are linked through bridging oxygen atoms. The pore system of ETS-10 contains 12-membered rings and displays a considerable degree of disorder. An additional difference between TS-1 and ETS-10 is that while the latter possesses significant cation exchange capacity, only negligible amounts of alkali cations can be exchanged into TS-1 (mostly by the surface silanols at defect sites). What are the consequences of the different structural connectivities (between TS-1 and ETS-10) on their catalytic behavior? The catalytic activity of TS-1 in oxidation reactions using H<sub>2</sub>O<sub>2</sub> as the oxidant is well known. Not much is known about the catalytic behavior of ETS-10. However, due to its ion exchange capacity, ETS-10 is expected to be active in acid-catalyzed reactions when the alkali ions are

exchanged for protons. ETAS-10, the titanoaluminosilicate analog, has been shown to possess, as expected, significant catalytic activity in typical acid-catalyzed reactions such as *m*-xylene isomerization and cumene cracking (2). In addition to the Ti<sup>4+</sup> ions, (the active sites for the oxidation reactions) TS-1 also possesses a significant amount of defect hydroxyl groups (about 20% for crystals of diameter 0.2 μm). Do these hydroxyl groups possess catalytic activity in those reactions which do not require strong acid sites (for example, double-bond isomerization)? We had, earlier, reported the excellent performance of TS-1 in the acid-catalyzed Beckmann rearrangement of cyclohexanone oxime to caprolactam (3), wherein the surface hydroxyls probably play a major role. It is of interest to further probe this novel aspect of the reactivity of TS-1 in nonoxidation reactions.

In the present paper, we study, by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, the nature and reactions of adsorbed 1-butene molecules, below monolayer coverage, on TS-1 and ETS-10. The kinetics of transformation of 1-butene has been evaluated from the variation of NMR intensities and compared with those obtained from conventional, fixed-bed catalytic reactor studies.

## EXPERIMENTAL

### Materials

TS-1 and ETS-10 were synthesized according to published procedures (Refs. (4) and (5), respectively). The as-synthesized TS-1 was dried (383 K) and calcined (773 K) in air prior to use. The ETS-10 was first subjected to cation exchange (NH<sub>4</sub>NO<sub>3</sub> solution {2.5%}, 368 K for 6 h, 6 times), dried at 383 K, and calcined in N<sub>2</sub> at 520 K, prior to use. It was confirmed (by DTA/TGA) that NH<sub>3</sub> removal was completed by this calcination process.

### Procedures

The chemical composition of the samples was determined by wet chemical methods and atomic absorption

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(Hitachi Model Z-8000). Their average particle sizes were determined by scanning electron microscopy (JEOL, JSM 5200). The UV-VIS diffuse reflectance spectra of TS-1 and ETS-10 were scanned using a Shimadzu (Model UV-2101PC) spectrometer. The crystallinity and phase purity of the samples were verified by X-ray diffraction (Rigaku, Model D-max III). The zeolite surface areas were determined by conventional volumetric adsorption using  $N_2$  at  $P/P_0$  values lower than 0.05 by the ASTM procedure D-4365-85 ("Determining zeolite area of a catalyst"). At these relative pressure values condensation in the pores is unlikely. (The values of both  $C$  and the intercept were positive). The BET surface area was not significantly different from the Langmuir area. The FTIR spectra were recorded with a Nicolet FTIR spectrometer (Model 60 XB). The catalytic reactions were carried out in a glass, fixed-bed reactor in the downflow mode. About 1.0 g of the catalyst powder (10–20 mesh) was held in position between inert porcelain chips. A mixture of 1-butene and pure  $N_2$  (1:2 by volume) was used as the reactant. Blank runs without any catalyst in the reactor and at the same reaction temperature revealed only negligible conversion of 1-butene (less than 0.1%) even at the highest temperature used in the present study. The reaction products were directly analyzed by capillary column gas chromatography (Hewlett Packard, Model 5880-A, Refinery gas analyzer). Reactant and products were identified and estimated using a refinery gas test sample (HP Part No. 5080.8755) as the standard reference. FTIR spectra of the surface hydroxyl groups were recorded on thin self-supporting wafers of TS-1/ETS-10 contained in a specially designed glass cell which could be heated and evacuated *in situ* in the spectrometer.

### NMR Spectroscopy

For recording the  $^1H$  MASNMR spectra of adsorbed 1-butene molecules, catalyst samples were contained inside Pyrex capsules which could be spun inside the MASNMR probe heads at speeds up to 1.0 kHz. The design of the capsule allowed the samples to be attached to a conventional adsorption system and dehydrated at 673 K under a pressure of  $10^{-5}$  Torr before adsorption of 1-butene. About 70 mg of TS-1 (or ETS-10) was usually taken in the NMR capsule. 1-Butene was adsorbed at 273 K for 30 min. The tube was then evacuated for 30 min to remove reversibly adsorbed material. After the adsorption of 1-butene on the sample was measured, the tube was sealed under vacuum while keeping the sample frozen to prevent the onset of the chemical reactions. The tube was then placed in the conventional zirconia rotor and packed properly using quartz wool. After each NMR experiment, the capsule containing the catalyst and adsorbate was taken out and heated in an oven at the re-

quired temperature for different lengths of time. The NMR spectra were then recorded.

The high resolution solid state  $^1H$  MASNMR spectra were acquired at 300.13 MHz, at a spinning speed of 0.8 kHz with a Bruker MSL-300 spectrometer. Due to the lower NMR intensity of the  $^{13}C$  compared to  $^1H$  (by a factor of  $10^4$ ) more sample (1.25 g) was needed to record the  $^{13}C$  NMR spectra and we could not use the capsule. Hence, magic angle spinning could not be done. The samples were filled in larger tubes (normally used for NMR of liquids) and adsorption measurements were done under conditions identical to those used with the capsule. The tubes were then sealed under vacuum and the NMR spectra were recorded under static conditions.  $^{13}C$  spectra were acquired at 75.476 MHz,  $4 \mu s$  ( $30^\circ$ ) pulses with a repetition time of 2 s and with broad band decoupling of protons during acquisition and recycle delay. Chemical shifts are referred to external tetramethyl silane (TMS) or liquid butenes. The proton spectra were recorded using  $5 \mu s$  ( $45^\circ$ ) pulses with a repetition time of 1 s. The proton data obtained with larger recycle delay showed similar signal intensity. All NMR spectra were recorded at room temperature. The deconvolution of the NMR spectra (to obtain the chemical shift parameters, intensities, and linewidths) was done using the software supplied along with the spectrometer (LINESIM).

## RESULTS AND DISCUSSION

### Catalyst Characterization

TS-1. The Si/Ti ratio in TS-1 was 30. The average particle size of the powder was about  $0.2 \mu m$  (SEM). The XRD pattern (similar to the MFI system), framework IR spectra (peak at  $960 \text{ cm}^{-1}$ ), UV-VIS diffuse reflectance spectra (Fig. 1), zeolite surface area ( $420 \text{ m}^2/\text{g}$ ), and significant catalytic activity in the oxidation of phenol to

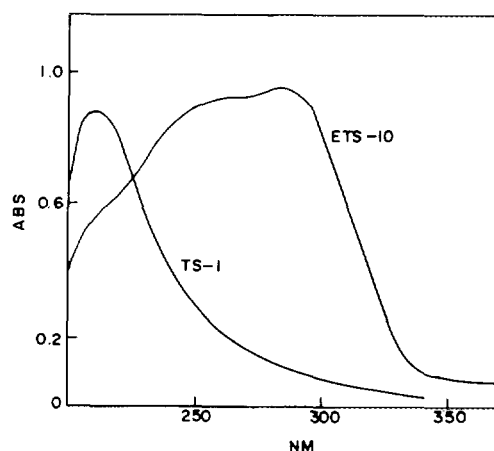


FIG. 1. UV-VIS diffuse reflectance spectra of TS-1 and ETS-10.

hydroquinone/catechol indicated that the sample was indeed TS-1 and similar to those used in our earlier studies on the Beckmann rearrangement reactions (3).

**ETS-10.** The chemical composition of the as-synthesized sample was 5.68 SiO<sub>2</sub>:TiO<sub>2</sub>:0.80 Na<sub>2</sub>O:0.20 K<sub>2</sub>O:3 H<sub>2</sub>O. After proton exchange it was 5.68 SiO<sub>2</sub>:TiO<sub>2</sub>:0.25 Na<sub>2</sub>O:0.005 K<sub>2</sub>O:2.9 H<sub>2</sub>O. The average particle size was around 3–4 μm (SEM). The X-ray diffraction pattern (Fig. 2) was similar to those published earlier for ETS-10 (5). The UV–VIS diffuse reflectance spectrum of ETS-10 is given in Fig. 1. The framework IR spectrum of ETS-10 is shown in Fig. 3. To our knowledge, this information has not been published before. The proton exchanged form (used for NMR and catalytic studies) had a zeolite surface area of 380 m<sup>2</sup>/g and adsorbed (at 298 K and  $P/P_0 = 0.5$ ) 16.9, 9.9 and 12.3 wt% of H<sub>2</sub>O, *n*-hexane, and 1,3,5-trimethylbenzene, respectively. These values are comparable (except for 1,3,5-trimethylbenzene) to 12.9, 8.2, and 0.5 wt%, respectively, reported for ETS-10 (5). It may, hence, be concluded that our ETS-10 is comparable to that of the original patent (5).

#### NMR Spectroscopy

**TS-1.** Figure 4 shows the progressive transformation of the <sup>1</sup>H MASNMR spectrum of 1-butene on TS-1 at 313 and 373 K. 1-Butene was adsorbed on TS-1 at 313 K. Assuming that each adsorbed 1-butene molecule occupies an area of 30 Å<sup>2</sup>, the fractional coverage,  $\theta$ , was estimated to be 0.73. The chemical shifts, in parts per million, downfield from TMS, are given in Table 1. The assignments in Table 1 have been made on the basis of values for liquid butenes and those observed for adsorption on other solids like Pt–Al<sub>2</sub>O<sub>3</sub> (7). As expected for protons, there were no significant changes in the chemical shift parameter with severity of treatment. For example, the chemical shift due to the =CH— group in

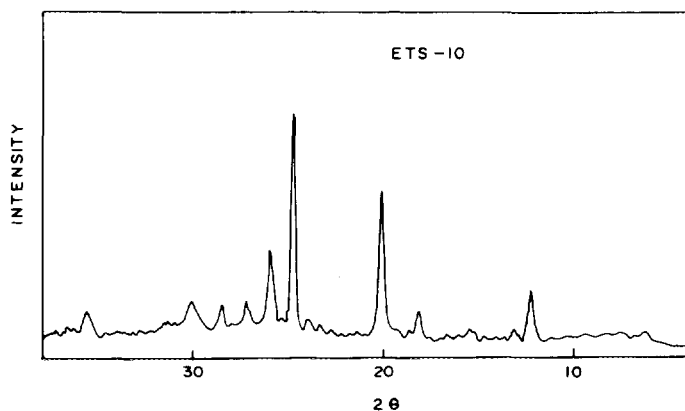


FIG. 2. X-ray diffraction pattern of ETS-10.

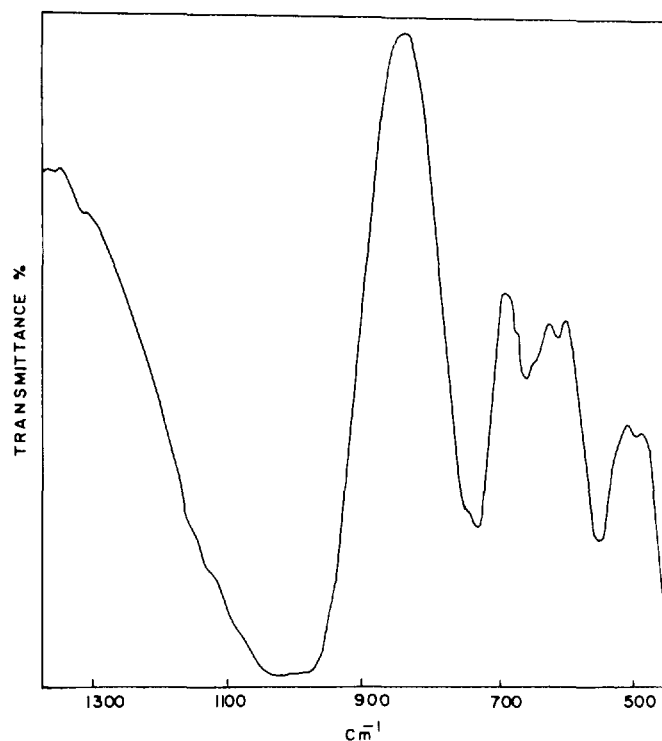


FIG. 3. Framework IR spectrum of ETS-10.

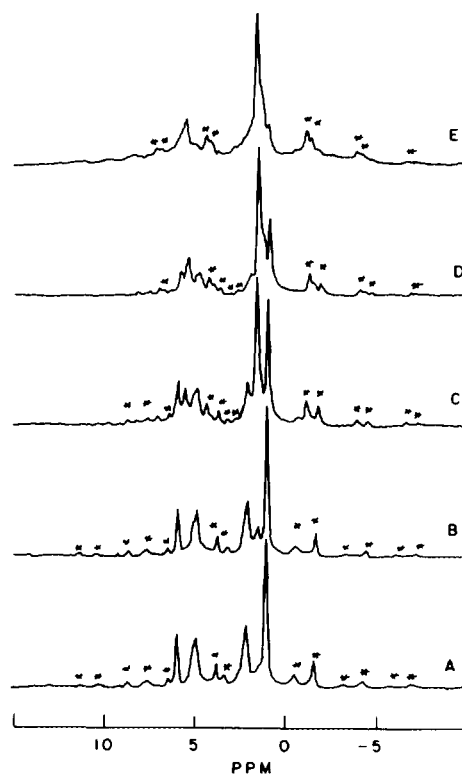


FIG. 4. <sup>1</sup>H MASNMR spectra of 1-butene remaining adsorbed on TS-1 at 313 K (curve A) and after heating at 373 K for 120, 840, 1140, and 1860 min (curves B–E, respectively). Spinning side bands are marked by asterisks.

TABLE 1  
<sup>1</sup>H MASNMR Chemical Shifts of Adsorbed Butenes

Chemical shift ( $\Delta \delta$ ) <sup>a</sup>		Functional group assignment
TS-1	ETS-10	
6.0	6.3	=CH— in 1-butene
5.1	5.5	=CH <sub>2</sub> in 1-butene
2.1	2.1	—CH <sub>2</sub> — in 1-butene
1.1	1.0	—CH <sub>3</sub> in 1-butene
1.7	1.5	—CH <sub>3</sub> in 2-butene ( <i>cis</i> + <i>trans</i> )
5.6	5.6	—CH— in 2-butene ( <i>cis</i> + <i>trans</i> )
1.4	—	—CH <sub>2</sub> — in butene oligomer

<sup>a</sup> Chemical Shift in ppm with reference to TMS.

1-butene pretreated at 313 K for 30 min and at 373 K for 120, 840, 1140, and 1860 min (Fig. 5) were 5.99, 6.01, 5.99, 6.02, and 5.98 ppm, respectively. The corresponding values for the =CH<sub>2</sub> group were 5.12, 5.11, 5.09, 5.21, and 5.21 ppm, respectively. The variation of the intensity of the various proton lines of Fig. 4 is brought out in more graphic detail in Fig. 5. The isomerization of 1-butene to 2-butene occurs already at 373 K, and with prolonged exposure to 373 K, the lines due to 1-butene diminish in intensity. Simultaneously those due to 2-butene are enhanced. The ratio of the *cis/trans* isomers among the 2-butenes was 0.70 (from area ratios of the <sup>13</sup>C NMR spectrum, discrepancies arising due to NOE effects are not considered). Beyond about 1000 min, increasing absorption in the aliphatic —CH<sub>2</sub>— and —CH<sub>3</sub> regions suggest that oligomerization of the adsorbed 1-butene molecules on the surface of TS-1 is probably taking place. The enhanced degree of chemical interaction between adsorbed 1-butene molecules and the TS-1 surface on prolonged exposure is also supported by the

increasing linewidth of all the proton lines due to 1-butene (Fig. 6). Conard *et al.* (7), for 1-butene on Pt-Al<sub>2</sub>O<sub>3</sub> observed <sup>1</sup>H NMR linewidths of about 100 Hz. Our values (Fig. 6) range from 60–140 Hz. If it is recalled that the surface coverage of 1-butene on our TS-1 sample was 0.73 at 313 K (and less at 373 K), we can conclude that a major fraction of the butene molecules interact directly with the surface of TS-1 and that the observed NMR spectra can be considered as representative of the chemisorbed phase. The increasing linewidth of the NMR lines (Fig. 6) is, hence, indicative of the progressively enhanced dipolar interaction between the <sup>1</sup>H spins of the adsorbed butene molecules and the nuclear spins on the surface of the solid. The latter are, perhaps, the protons of the surface (OH) groups. It may be noted that the concentration of paramagnetic metallic impurities in our samples was negligible due to the high purity of the raw materials used (tetraethyl orthosilicate and titanium butoxide from Aldrich, USA).

The <sup>13</sup>C NMR spectra of 1-butene adsorbed at 313 K on TS-1 and heated progressively to higher temperatures are shown in Fig. 7. The spectra were recorded at room temperature under static (no MAS) conditions. The chemical shifts of the major peaks and their probable assignments are given in Table 2. The variation of the line intensities is given in Fig. 8. The <sup>13</sup>C NMR spectra of 1-butene adsorbed on various solids has been studied very extensively (8). Nagy *et al.* (9) studied the isomerization of 1-butene on NaGeX and proposed that the isomerization occurs at 573 K via a cyclic transition state involving the butene molecule and the simultaneous presence of an acidic and a basic site on the surface. More recently, Basini *et al.* (10) investigated this reaction over silica-alumina by IR spectroscopy and proposed that reversible proton transfer reactions between surface OH groups and

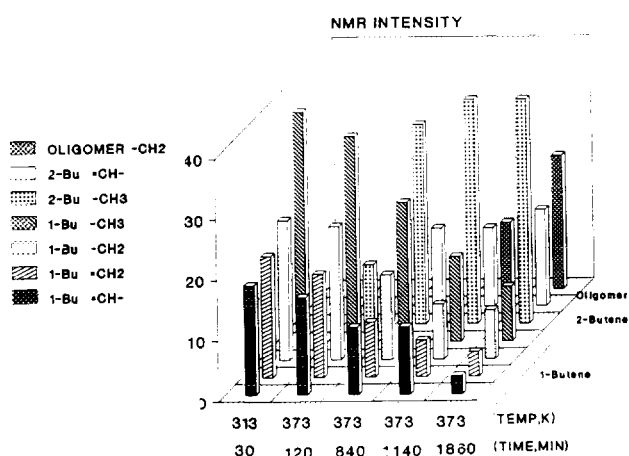


FIG. 5. <sup>1</sup>H MASNMR of adsorbed 1-butene on TS-1, variation of intensity with pretreatment.

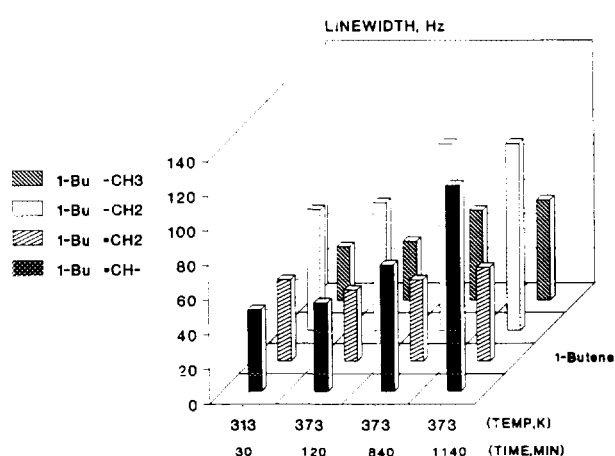


FIG. 6. Linewidth variations of the <sup>1</sup>H MASNMR bands of 1-butene adsorbed on TS-1.

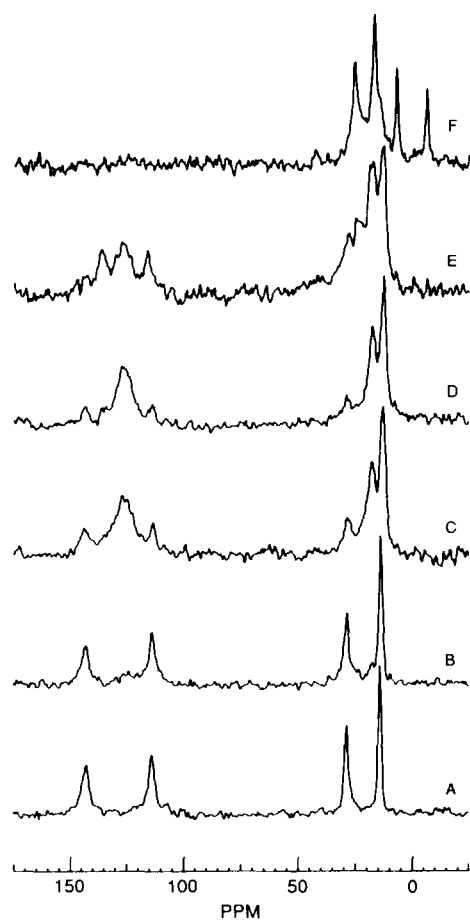


FIG. 7.  $^{13}\text{C}$  NMR spectra of 1-butene remaining adsorbed on TS-1 at 313 K (curve A), after heating at 473 K for 600 min (curve B) and at 573 K for 60, 120, 240, and 540 min (curves C–F, respectively).

TABLE 2

$^{13}\text{C}$  NMR Chemical Shifts of Adsorbed Butenes

Chemical shift ( $\Delta \delta$ ) <sup>a</sup>		Functional group assignment
TS-1	ETS-10	
143.4 (3.2)	148.1 (7.9)	$=\text{CH}-\text{H}$ in 1-butene
113.8 (0.8)	113.5 (0.5)	$=\text{CH}_2$ in 1-butene
28.8 (1.9)	29.2 (2.3)	$-\text{CH}_2-$ in 1-butene
14.3 (1.4)	14.6 (1.1)	$-\text{CH}_3$ in 1-butene
13.5 (2.6)	13.8 (2.9)	$-\text{CH}_3$ in 2-butene ( <i>cis</i> )
18.5 (1.5)	18.1 (1.1)	$-\text{CH}_3$ in 2-butene ( <i>trans</i> )
126.1 (2.8)	129.9 (6.6)	$=\text{CH}-$ in 2-butene ( <i>cis</i> )
126.1 (11.5)	129.9 (15.3)	$=\text{CH}-$ in 2-butene ( <i>trans</i> )

Note. Values in parentheses refer to the shift relative to the liquid state.

<sup>a</sup> Chemical shift in ppm with reference to TMS.

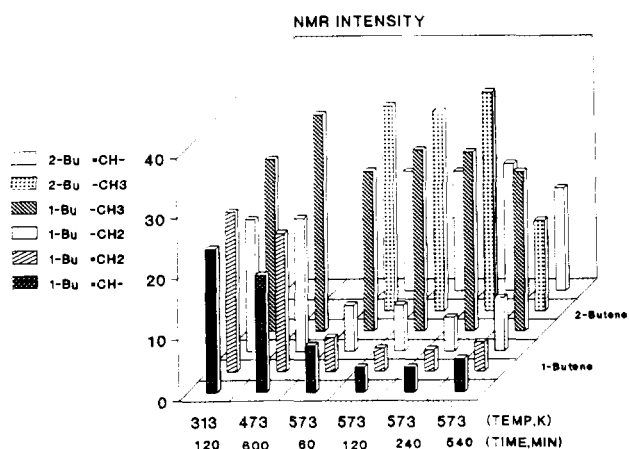


FIG. 8.  $^{13}\text{C}$  NMR of adsorbed 1-butene on TS-1, variation of intensity with pretreatment.

the double-bond carbon atoms of the butene catalyze the isomerization. At 573 K and on the nonacidic NaGeX sample, Nagy *et al.* (9) determined the kinetics of 1-butene isomerization to 2-butene from the variation of the NMR intensities. Isobutene, arising by skeletal isomerization was not observed. From the data in Figs. 5 and 8 we calculated the pseudo-first-order rate constants for the reaction of 1-butene by a procedure similar to that of Nagy *et al.* (9) Figure 9 shows the kinetic plots ( $\ln c/c_0$  vs time) for the disappearance of the four characteristic  $^1\text{H}$  MASNMR peaks of 1-butene at 373 K. The values of the pseudo-first-order rate constants at 373 and 573 K were  $3.8 \times 10^{-4}$  and  $25 \times 10^{-4} \text{ min}^{-1}$ , respectively. The latter value is in excellent agreement with that of Nagy *et al.*

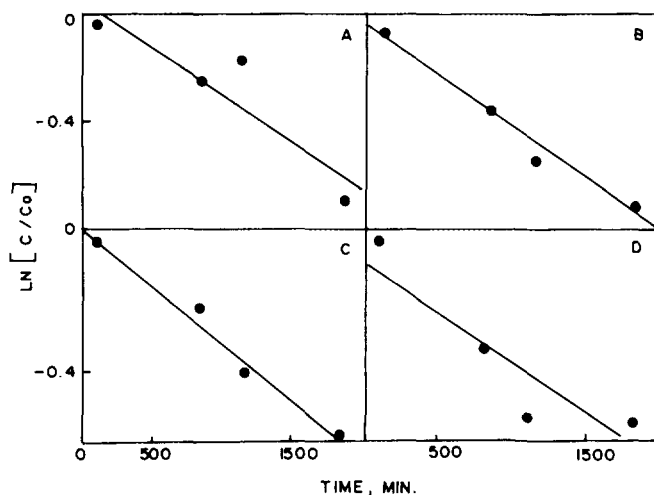


FIG. 9. Kinetic plots from variation (at 373 K) of the intensity of the  $^1\text{H}$  MASNMR peaks of 1-butene; A–D refer to the functional groups,  $=\text{CH}-$ ,  $=\text{CH}_2$ ,  $-\text{CH}_3$ , and  $-\text{CH}_2-$ , respectively.

( $23 \times 10^{-4} \text{ min}^{-1}$ ) at the same temperature. The nonacidic nature of both TS-1 and NaGeX (from Nagy *et al.* (9)) is probably the reason for this agreement. For the more acidic NaHGeX, Poncelet *et al.* (11) measured a value of  $115 \times 10^{-4} \text{ min}^{-1}$  for the apparent first-order kinetic rate constant in agreement with expectations. The values from the three studies are reasonably consistent.

An interesting observation in Fig. 7 is the peak *upfield* of TMS at  $-6.8 \text{ ppm}$  (curve F, Fig. 7) observed in the case of a TS-1 sample exposed to 1-butene and heated at 573 K for 35 h. This peak (which is not a spinning side band) was not observed in earlier studies with other catalyst systems. Shifts in the  $^{13}\text{C}$  NMR upfield of TMS are usually observed in methylene heterocycles wherein the carbon atom is attached to Si, Ge, or Sn (12). The peak at  $-6.8 \text{ ppm}$  can also arise from adsorbed methane species. However, there is a lower probability that adsorbed  $\text{CH}_4$  will be present in samples heated at 573 K.

**ETS-10.** The  $^{13}\text{C}$  NMR spectra of 1-butene adsorbed on the proton form of ETS-10 ( $\theta = 0.6$ ) is shown in Fig. 10. A tentative assignment of the NMR peaks to the functional groups of the adsorbed molecules is shown in Table 2. The downward chemical shifts of the  $=\text{CH}-$  groups in both 1- and 2-butenes are more pronounced in the case of ETS-10 than in the case of TS-1 (7.9 vs 3.9 for 1-butene and 6.6 and 15.3 vs 2.8 and 11.5 ppm for *cis*- and *trans*-2-butenes, respectively). Due to the relatively greater acidity of ETS-10, the isomerization of 2-butene occurs already at room temperature, in contrast to TS-1. Over the latter, detectable isomerization takes place only at 373 K and even then only on prolonged exposure (Fig. 4). On raising the temperature to 373 K, the peaks in the olefinic carbon range (100–150 ppm) decrease drastically with a simultaneous intensity increase (Fig. 10) in the aliphatic  $-\text{CH}_3$  and  $-\text{CH}_2$  region (0–50 ppm), probably due to the oligomerization of the adsorbed butene molecules. We could not do a satisfactory quantitative deconvolution of the peaks in Fig. 10 due to the overlap of the peaks of 1- and 2-butenes (and possibly even the oligomer) in all the spectra including that recorded at room temperature.

Figure 11 illustrates the  $^1\text{H}$  MASNMR of adsorbed 1-butene on ETS-10 and heated to various temperatures. The  $^1\text{H}$  chemical shifts of the principal functional groups are listed in Table 1. The isomerization (to 2-butene) occurs already at 313 K, in agreement with  $^{13}\text{C}$  NMR results. A general observation is that spinning side bands are more prevalent with ETS-10 than TS-1. Due to this, satisfactory deconvolution of the NMR peaks in Fig. 11 (to obtain the intensities and linewidths of the lines) could not be carried out. At 383 K and above the lines due to the oligomerized species with chemical shifts in the region 0.5–3.0 ppm could also be detected. The results in Fig. 11 are, hence, in broad agreement with those of Fig.

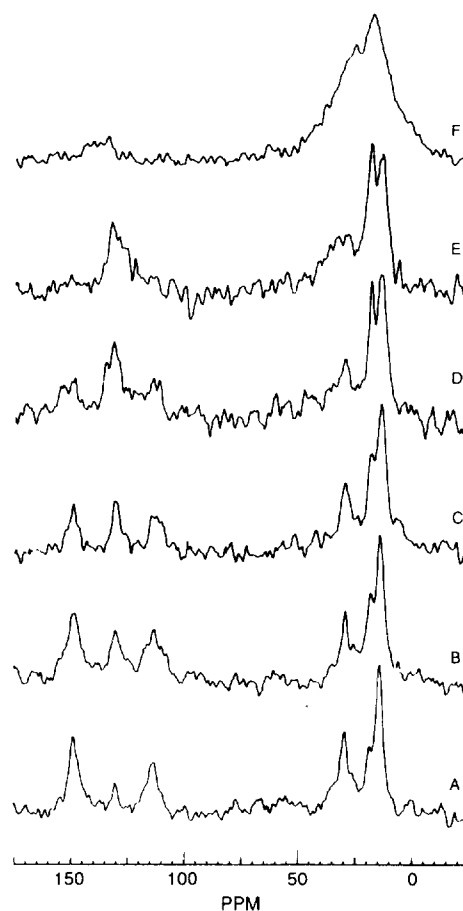


FIG. 10.  $^{13}\text{C}$  NMR spectra of 1-butene remaining adsorbed on ETS-10 at 313 K for 300, 660, 960, 1500, and 2280 min (curves A–E, respectively) and after heating at 383 K for 120 min (curve F).

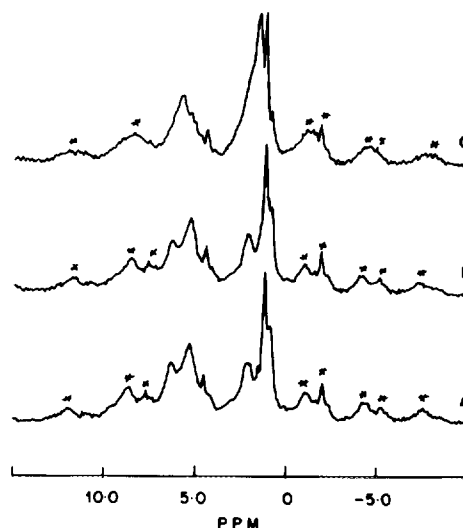


FIG. 11.  $^1\text{H}$  MASNMR spectra of 1-butene remaining adsorbed on ETS-10 at 313 K (curve A), after heating at 333 K for 60 min (curve B) and at 383 K for 60 min (curve C). Spinning side bands are marked by asterisks.

10 ( $^{13}\text{C}$  NMR of 1-butene on ETS-10) and indicate a greater interaction of the butene molecules with the surface of ETS-10 than with that of TS-1.

It may be mentioned here that neither isobutene nor any cracked products due to C–C fission were observed by NMR spectroscopy either on TS-1 or on ETS-10. These products were not detected in the conventional catalytic experiments either (described later). Apparently, these catalysts are selective for double-bond isomerization. However, they possess only a low level of activity for olefin isomerization compared to other conventional catalysts (like zeolites or amorphous silica-alumina).

### FTIR Spectroscopy

The FTIR spectra of surface hydroxyl groups in dehydrated samples of TS-1 and ETS-10 are shown in Fig. 12. The IR bands at 1640  $\text{cm}^{-1}$  characteristic of molecular water are not observed. The peak around 3735  $\text{cm}^{-1}$  is due to isolated terminal silanol groups. The sharp peak at 3700  $\text{cm}^{-1}$  observed on ETS-10 is probably due to isolated Ti–OH groups. Their concentration is much lower on TS-1. The broad band around 3200–3600  $\text{cm}^{-1}$  is probably due to H-bonded surface hydroxyl groups of both Si and Ti. They are similar to the (OH) groups observed by us earlier for VS-1, the vanadium silicate analog of TS-1 (13),

the concentration of which was found to increase with the amount of vanadium in the molecular sieve. These are presumably the (OH) groups present at the surface defect sites. The influence of such (OH) groups on the catalytic properties of materials such as TS-1 and VS-1 is not well understood, at present. When pyridine was adsorbed on TS-1 at 300 K and the system evacuated at 473 K no adsorbed pyridine was detected on the surface. The acidity of the sites on TS-1 is weak, as expected.

### Catalytic Reaction Studies

The isomerization of 1-butene on TS-1 and ETS-10 was also studied in a conventional fixed bed reactor (see Experimental). The conversion of 1-butene was kept below 10–15%. The temperature dependence of the apparent rate constants (for the disappearance of 1-butene) is shown in Fig. 13. The *cis/trans* ratio among the 2-butenes was 0.62. Apparent activation energies for TS-1 and ETS-10 in the range 573–673 K are calculated to be 12 and 4 kcal/mole, respectively. The latter value, perhaps, indicates that, over ETS-10, some transport phenomenon rather than a chemical transformation step may be involved in the rate-determining step. In view of the larger particle size (3–4  $\mu\text{m}$ ) and the relatively higher acidity of ETS-10, and its consequent higher catalytic activity, this is not so surprising. Moreover, since the conversions were below 15%, it is unlikely that the lower apparent activation energy arises from equilibrium limitations. A comparison was also made with the apparent activation energy for the reaction calculated from the temperature dependence of the NMR intensity of the  $^{13}\text{C}$  NMR lines in the case of TS-1. A value of 9 kcal/mole was obtained in reasonable agreement with that (12 kcal/mole) obtained from the catalytic reactor tests, again confirming that the species observed in the NMR spectra are indeed chemisorbed 1-butene molecules in intimate chemical interaction with the solid surface. The acidity in ETS-10 is related to its significant cation exchange capacity. When part of the alkali cations are replaced with protons by ion exchange, the material exhibits Brønsted acidity. The origin of acidity in TS-1 is not clear, at present. While trace impurities (like  $\text{Al}^{3+}$ ) in the raw material may contribute to the observed acidity, another possibility is that  $\text{Ti}^{4+}$  ions are reduced to  $\text{Ti}^{3+}$  by the hydrocarbon molecules during the reaction (especially at elevated temperatures) and thereby generate acid sites (similar to  $\text{Al}^{3+}$  in aluminosilicates). An esr signal is usually seen (due to  $\text{Ti}^{3+}$ ) when TS-1 is contacted with  $\text{H}_2$  at high temperatures.

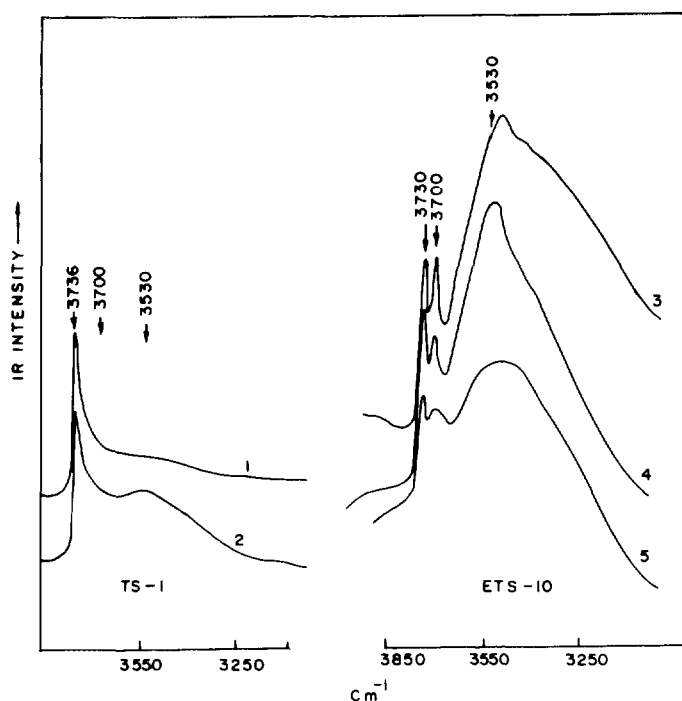


FIG. 12. IR spectra of silicalite and TS-1 evacuated at 573 K (curves 1 and 2, respectively) and ETS-10 evacuated at 313, 373, and 473 K (curves 3–5, respectively).

### SUMMARY AND CONCLUSIONS

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 1-butene molecule adsorbed (below monolayer coverage) on TS-1 and ETS-10 have been studied. The downfield chemical shifts of

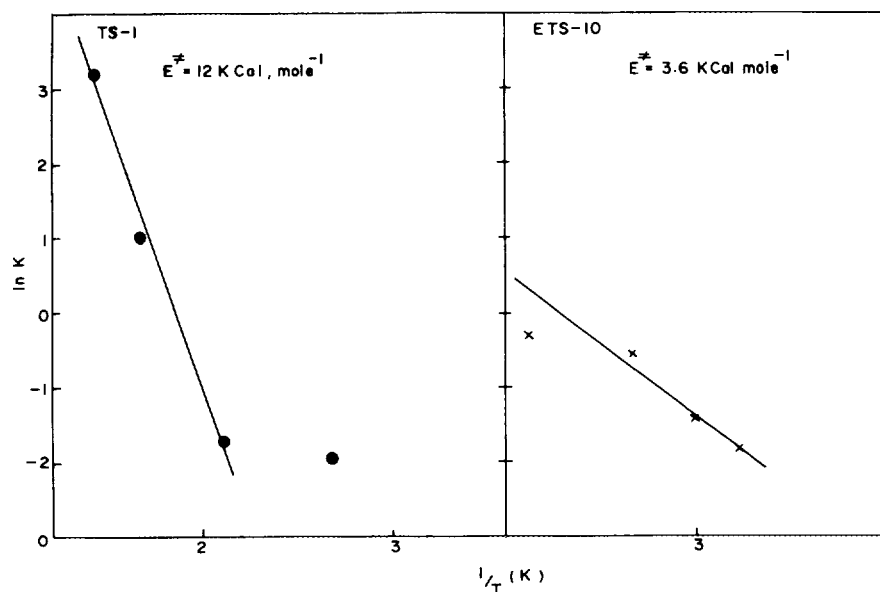


FIG. 13. Apparent activation energy plots for the transformation of 1-butene on TS-1 and ETS-10.

<sup>13</sup>C atoms are more pronounced in the case of ETS-10 than in the case of TS-1, indicating a stronger interaction with the more acidic surface of the former. ETS-10 is more active than TS-1 in the isomerization of 1-butene. The kinetic parameters of double-bond isomerization of 1-butene have been calculated from changes in the intensity of the NMR lines and compared with those obtained from conventional catalytic reactor studies. Satisfactory agreement between the two values is observed. The observed NMR spectra are, hence, indeed those of chemisorbed butene molecules undergoing chemical transformation. Both TS-1 and ETS-10 are highly selective catalysts for double-bond isomerization of 1-butene to 2-butene. Both isobutene (arising by skeletal isomerization) and cracked products (from C–C fission) are absent among the products. Along with our earlier report (3) on the superior performance (activity, selectivity, and stability) of TS-1 in the Beckmann rearrangement of cyclohexanone oxime to caprolactam, the present study focuses attention on aspects of the catalytic activity of these titanosilicate molecular sieves, which are not widely studied. In addition to the titanium atoms (the role of which in oxidation reactions has been well established) these materials also contain a large concentration of surface hydroxyl groups (observed by IR spectra, Fig. 12) at surface defect sites. These hydroxyl groups as well as the coordinatively unsaturated surface Si<sup>4+</sup> ions generated from them are probably the potential active sites in reactions like the Beckmann rearrangement and double-bond isomerization.

#### ACKNOWLEDGMENTS

We thank the European Commission (Contract C11-CT93-0361) for partial financial support.

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