

# Acid Property of Silanol Groups on Zeolites Assessed by Reaction Probe IR Study

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Received May 24, 1999; revised September 1, 1999; accepted November 1, 1999

Silanol groups existing on the outer surfaces of zeolites, whose OH stretching band appears at the same frequency as that of silanol groups on amorphous silica, are recognized as neutral or very weakly acidic. No significant difference in acidity between silanol groups on zeolites and those on amorphous silica has yet been found by studying the adsorption of probe molecules. However, it was found by a "reaction probe IR study" that silanol groups involved in highly crystallized structures of zeolites (ferrierite and ZSM-5) donated their protons to olefins (2-methylpropene, 2,4,4-trimethyl-1-pentene, and 2,4,4-trimethyl-2-pentene) at temperatures lower than 220 K, in contrast to those on amorphous silica. The products formed from reaction of those olefins with silanol groups were identical to 2,4,4-trimethyl-2-pentoxy groups ((CH<sub>3</sub>)<sub>3</sub>C-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-O-Si). These results suggest a difference in acidity between silanol groups on zeolites and those on amorphous silica. © 2000 Academic Press

**Key Words:** silanol groups, zeolites, olefin, IR.

## INTRODUCTION

In general, various acid-catalyzed reactions on zeolites are known to proceed on the strong Brønsted acidic OH groups bridging Si and Al atoms in zeolite pores (1). On the other hand, the silanol groups existing on the external surfaces of zeolites exhibit an OH stretching band at the same frequency as that of amorphous silica, and their acidic properties have not been discussed. However, in some cases, such as Beckmann rearrangement on high silica ZSM-5, a catalytic role of silanol groups on zeolites has been proposed (2). In the course of our series of IR studies of olefin adsorption on zeolites, we noticed the reaction of silanol groups on zeolites with some olefins (3, 4), which has not yet been systematically investigated. Especially in the case of reactions between large olefins and zeolites with relatively small micropores (ferrierite and ZSM-5), considerable energy barriers restrained the intrusion of bulky olefins into the small pores. Instead, the reaction of olefins

with silanol groups on the external surfaces of zeolites was clearly observed (3, 4). In this study, the reactivity (availability of protonation) of silanol groups existing on the external surface of various zeolites toward various reactants was carefully examined by IR spectroscopy. The differences between silanol groups on zeolites and those of silanol groups on amorphous silica in acidity and reactivity are experimentally demonstrated.

## EXPERIMENTAL

Ferrierite zeolite (Tosoh Corp., Si/Al = 8.5), H-ZSM-5 (Sumitomo Chemical Co. Ltd., Si/Al = 50), and amorphous silica (Aerosil Nippon) were used as received. About 20–40 mg of each catalyst was pressed into a self-supporting disk and then placed in a quartz cell connected to a conventional closed gas-circulation system. Sample disks of ferrierite, H-ZSM-5, and silica were pretreated at 773 K with exposure to O<sub>2</sub> gas (100 Torr, 1 Torr = 133.322 Pa) on a liquid nitrogen trap for 1 h and then evacuated at the same temperature for 15 min. To confirm the isotope shift between OH and OD bands, acidic OH groups on samples were in some cases deuterated at 673 K with 100 Torr of D<sub>2</sub> (purity >99.95%) for 0.5–1 h. Zeolites are well known to have Brønsted and Lewis acid sites; however, the pretreatment conditions were chosen to produce no Lewis acid sites on the catalysts. The absence of Lewis acid sites was confirmed using CO molecules as a probe (5, 6). The IR spectra of ferrierite before and after CO adsorption are shown in Figs. 1a and 1b, respectively. The spectrum obtained by subtraction of (a) from (b) is also shown in Fig. 1c for clear detection of the spectral change upon CO adsorption. The external silanol groups and the acidic hydroxy groups were observed at 3750 and 3608 cm<sup>-1</sup> (2764 and 2262 cm<sup>-1</sup> for corresponding OD groups), respectively, after the pretreatment. The involvement of the acidic OH and OD groups in CO adsorption was confirmed by the shifts of their bands from the isolated (3609 and 2663 cm<sup>-1</sup>) positions to the hydrogen-bonded (3317 and 2468 cm<sup>-1</sup>) positions. The hydrogen-bonded CO showed a band at 2172-cm<sup>-1</sup>,

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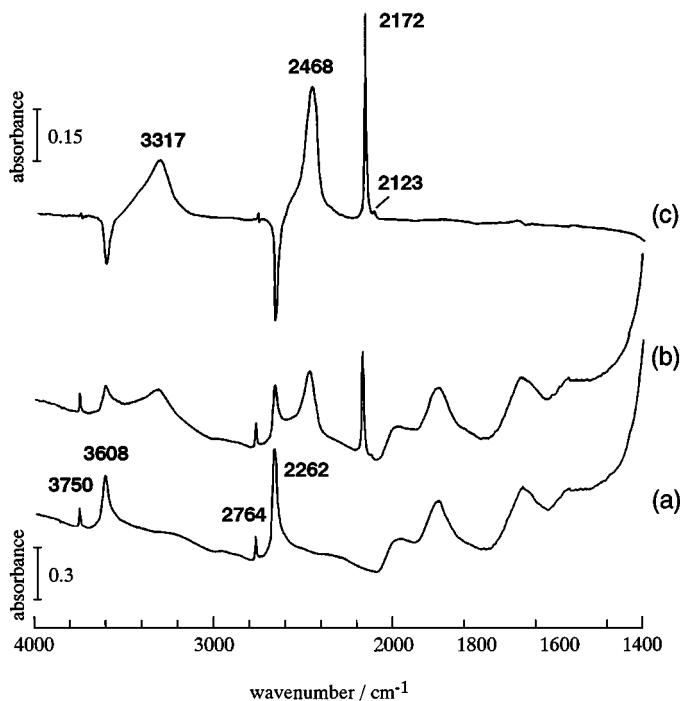


FIG. 1. IR spectra of ferrierite (a) before and (b) after adsorption of CO. Spectrum (c) was obtained by subtracting spectrum (a) from (b). CO (1.5 Torr) was introduced and evacuated at 203 K.

while the band at  $2123\text{ cm}^{-1}$  is attributed to the physically adsorbed CO. In general, CO adsorbed on to Lewis acid sites of zeolites or strongly cationic sites of oxides is known to show the CO stretching band at a higher frequency than hydrogen-bonded CO. The absence of such

a band in Fig. 1c indicates that no Lewis acid sites existed on the ferrierite zeolite under the present experimental conditions. Similarly, Lewis acid sites were not detected on H (D)-ZSM-5 by CO adsorption in the present study.

The existence of silanol groups and the absence of acidic OH groups on the external surface of ferrierite were confirmed by pyridine adsorption. In Fig. 2A as-observed spectra before (a) and after (b) probe adsorption, as well as the difference spectrum (c), are shown. The band attributed to silanol groups almost disappears, while that due to the acidic OH groups stays unchanged. These are clearly observed in the difference spectrum, where the consumed isolated silanol groups showed a sharp negative band, but the bands of the acidic OH groups shifted slightly (differential peak shape). Since the experiment was conducted at 235 K in order to avoid the thermal diffusion of pyridine into the pores, pyridine molecules adsorbed on silanol groups by hydrogen bonding. Consequently, a broad hydrogen-bonded silanol band was observed around  $3000\text{ cm}^{-1}$ , as well as bands due to molecular pyridine in the CH stretching region higher than  $3000\text{ cm}^{-1}$  and in the ring-breathing vibration region at  $1400\text{--}1610\text{ cm}^{-1}$  (7, 8). The small pore size of ferrierite inhibited the access of large pyridine molecules to the acidic OH groups, and the strong basicity of pyridine resulted in adsorption on the external silanol groups. Therefore, all the acidic OH groups were assigned to be inside the small pores of ferrierite. When ethene was used as a probe, ethene molecules irreversibly adsorbed exclusively on the acidic OH groups (Fig. 2B). Accordingly, it is possible to estimate the numbers of the

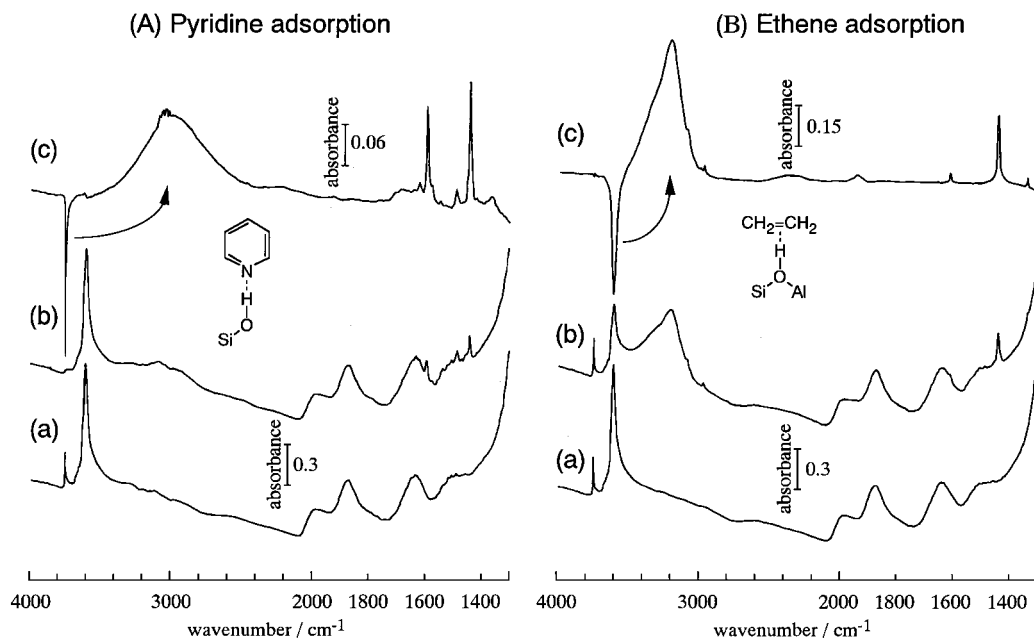


FIG. 2. (A) IR spectra of pyridine adsorbed on ferrierite at 235 K. (B) IR spectra of ethene adsorbed on ferrierite at 221 K. In both series, spectra (a) and (b) were measured before and after adsorption, respectively, and (c) represents the difference spectrum.

external silanol groups and the acidic OH groups by using pyridine and ethene adsorption. The numbers of silanol groups and acidic OH groups on the ferrierite used in the present study after the pretreatment described above were estimated by titration to be  $1.18 \times 10^{-4}$  and  $1.75 \times 10^{-3}$  mol  $g^{-1}$ , respectively.

2-Methylpropene (isobutene, Takachiho Trading Co., Ltd., 99.0% purity) was purified by vacuum distillation and freeze-pump-thaw cycles. D<sub>2</sub> (Takachiho Trading Co., Ltd., 99.99% purity) was purified before deuteration of the mordenite zeolite by repeatedly passing it through a liquid nitrogen trap. 2,4,4-Trimethyl-1-pentene (97% purity) and 2,4,4-trimethyl-2-pentene (99% purity) were purchased from Aldrich Chemical Co., Inc., and also purified by vacuum distillation and freeze-pump-thaw cycles before use.

The IR spectra were obtained by use of a JASCO 7300 FT-IR spectrometer equipped with an MCT detector at a resolution of 4  $cm^{-1}$ . Sixty-four scans were collected to obtain each spectrum. IR spectra of the clean disk were recorded under evacuation at various temperatures and were used as background spectra. IR spectra with the background spectra subtracted from those of the adsorbed species are shown in this paper unless otherwise noted as "as-observed spectra." The temperature, which was monitored with a thermocouple attached near the sample, was controlled by either cooling with a liquid nitrogen flow or by electrical heating, and it was calibrated to the real temperature of the sample disk using calibration curves between the apparent temperature and the real one.

## RESULTS AND DISCUSSION

### Adsorption and Reaction of Isobutene on Ferrierite and Silica

We have studied the adsorption and reaction of isobutene on the acidic OH groups of various acid catalysts including mordenite, ZSM-5, Y zeolites, and silica-alumina (3, 4). The reaction products were all assigned to dimeric alkoxy groups (2,4,4-trimethyl-1-pentoxy groups or 2,4,4-trimethyl-2-pentoxy groups) with a small amount of dimer olefin (2,4,4-trimethyl-1-pentene). In our studies, it was found that the acidic OH groups in the small micropores of ferrierite were not accessible by isobutene molecules below 250 K. Furthermore, the observed species were not attributed to molecularly adsorbed isobutene but were assigned to already dimerized species which adsorbed on sites other than the acidic OH groups. In such a case, consumption of the silanol groups existing on the external surface of ferrierite was found, which is shown below.

Figure 3 shows the as-observed spectra of ferrierite before (Fig. 3a) and after (Figs. 3b–3d) adsorption of isobutene at temperatures below 220 K. Spectra were measured throughout the warming procedure under evacuation after

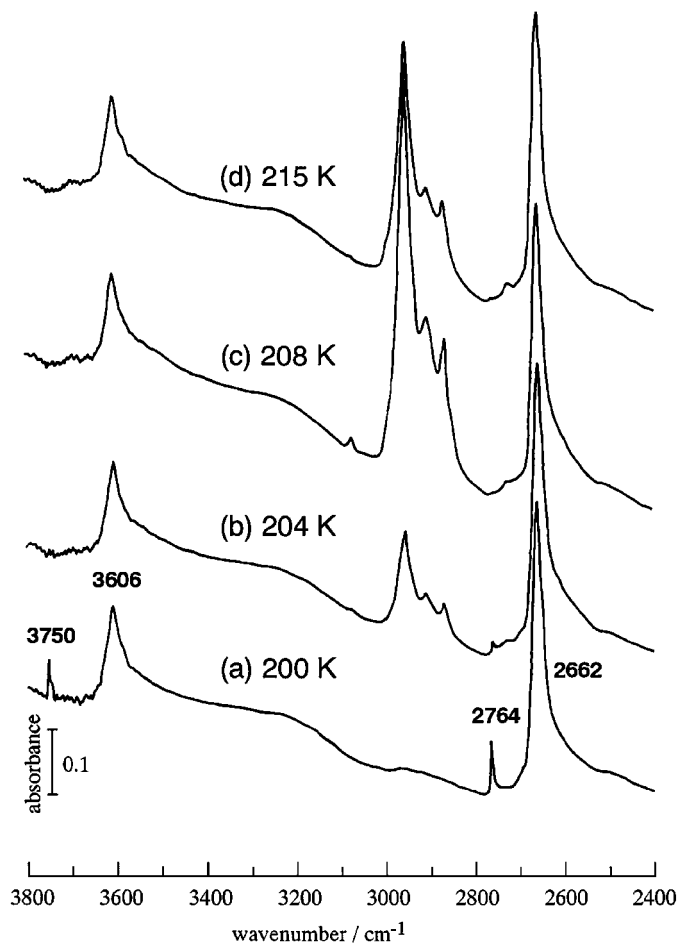
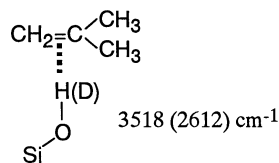


FIG. 3. As-observed IR spectra of ferrierite zeolite before and after isobutene adsorption. Spectra were measured at (a) 200 K before isobutene adsorption, (b) 204 K, (c) 208 K, and (d) 215 K after isobutene adsorption.

adsorption of  $2.3 \times 10^{-5}$  mol of isobutene. (The amount of silanol groups was estimated to be  $2.2 \times 10^{-6}$  mol for this sample.) In the spectrum of ferrierite before adsorption of isobutene (Fig. 3a), silanol and Brønsted acidic OH (OD) groups were observed at 3750 (2764) and 3608 (2662)  $cm^{-1}$ , respectively. After adsorption of isobutene (spectra (b)–(d) in Fig. 3), a decrease of the bands attributed to silanol groups was observed, while the bands due to the Brønsted acidic sites which exist in the pores of ferrierite remained unchanged. This indicates that isobutene could not intrude inside the pores of ferrierite but that it adsorbed onto the silanol groups on the outer surface. Ethene and propene could access the acid sites without a noticeable energy barrier at temperatures below 200 K, while considerable activation energies were required for linear butene molecules to access the acid sites. Moreover, a remarkable difference in activation energies for adsorption of 1-butene, *cis*-2-butene, and *trans*-2-butene on the acidic OH groups of ferrierite was found, which was due to their diffusion into the pores (9).

Therefore, it is well expected that the acidic OH groups in the ferrierite pores are not available for bulkier isobutene molecules at temperatures below 220 K.

The spectra with the background subtracted after isobutene adsorption are shown in Figs. 4b and 4c. Figure 4a is a reference IR spectrum for isobutene adsorbed on the silanol groups of amorphous silica. When isobutene was adsorbed on silica, molecularly adsorbed isobutene on silanol groups was observed, which simply desorbed by 230 K during heating under evacuation. The negative bands at 3752 and 2765  $\text{cm}^{-1}$  are attributed to the decreased isolated OH and OD groups due to interaction with the adsorbed isobutene, which shifted to 3518 and 2612  $\text{cm}^{-1}$ , respectively:



molecularly adsorbed isobutene on silanol groups on amorphous silica

All the other bands in Fig. 4a were assigned to the adsorbed isobutene molecules: an olefinic CH stretching band at 3079  $\text{cm}^{-1}$ , the other CH stretching bands in 2800–3000  $\text{cm}^{-1}$ , C=C stretching (1651  $\text{cm}^{-1}$ ), and some  $\text{CH}_3$  deformation and  $\text{CH}_2$  wagging bands in 1300–1500  $\text{cm}^{-1}$  region (10, 11). On the other hand, a considerably different spectrum for the species adsorbed on ferrierite at a lower temperature (208 K) was clearly observed in Fig. 4b, where the background spectrum in Fig. 3a was subtracted from the spectrum in Fig. 3c. The absence of adsorption on the acidic OH or OD groups was also confirmed by the lack of a negative OH or OD band due to the isolated acidic sites. Therefore, it was found that isobutene molecules could not adsorb on the acidic OH groups, and that a reaction occurred when they adsorbed on silanol groups at 208 K. After the temperature under evacuation was increased (Fig. 4c), about one-third of the IR absorption due to the adsorbed species decreased, maintaining the same spectral feature as in Fig. 4b. This is attributed to the desorption (or decomposition) of the adsorbed species. No noticeable H/D isotope exchange reaction was observed in the temperature range studied. The lack of any CD stretching band such as was supposed to appear in the 2100–2200  $\text{cm}^{-1}$  region (omitted in the spectra) is probably due to the small concentration of D atoms as well as the small absorption coefficient of the CD.

#### Assignment of the Product of the Reaction of Isobutene with Silanol Groups on Ferrierite

It was found in our previous studies that isobutene, being hydrogen-bonded to the acidic OH groups of solid acids (mordenite, ZSM-5, and Y zeolites as well as silica-

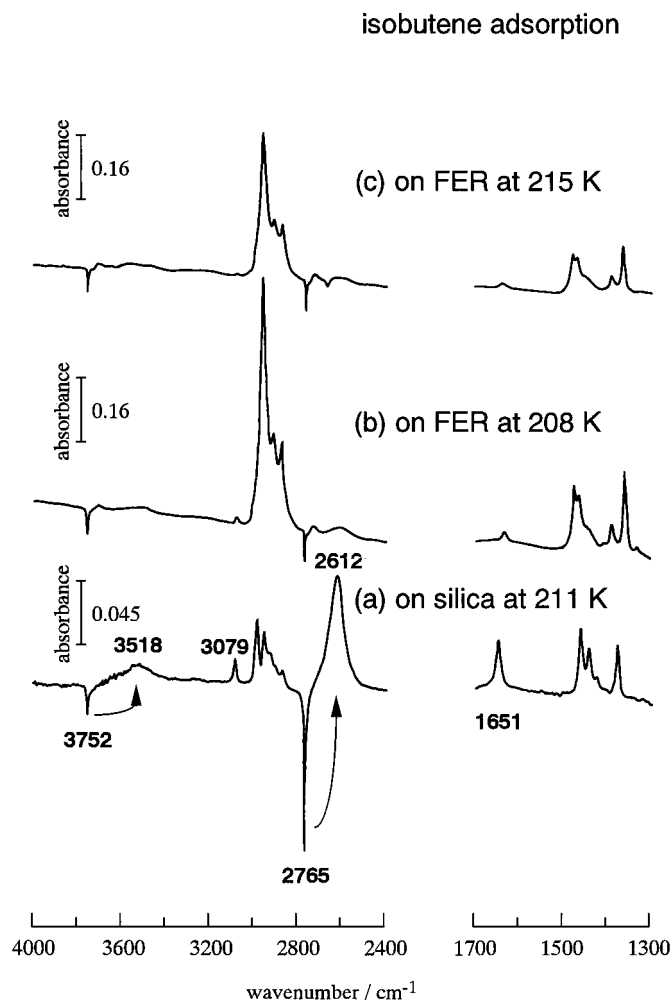
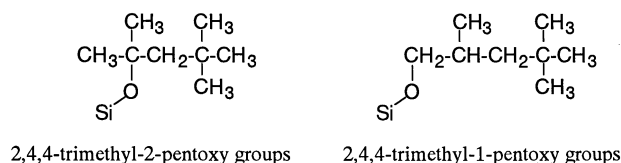


FIG. 4. IR spectra of isobutene adsorbed (a) on silica at 211 K, (b) on ferrierite at 208 K, and (c) on ferrierite at 215 K.

alumina), dimerized around 200 K even with a small amount of adsorbed molecules (less than 10% occupation of the acidic OH groups). The main dimerized product was identified as 2,4,4-trimethyl-2-pentoxo groups on the acidic OH groups of mordenite and Y-type zeolites as well as those of silica-alumina, with a small amount of 2,4,4-trimethyl-1-pentene, where no steric hindrance existed, while 2,4,4-trimethyl-1-pentoxo groups were selectively formed on the acidic OH groups of ZSM-5 (3, 4):



On the basis of these observations, we suspected the product of isobutene on the silanol groups of ferrierite (Fig. 4) to be the dimerized species also. Therefore, IR spectra of

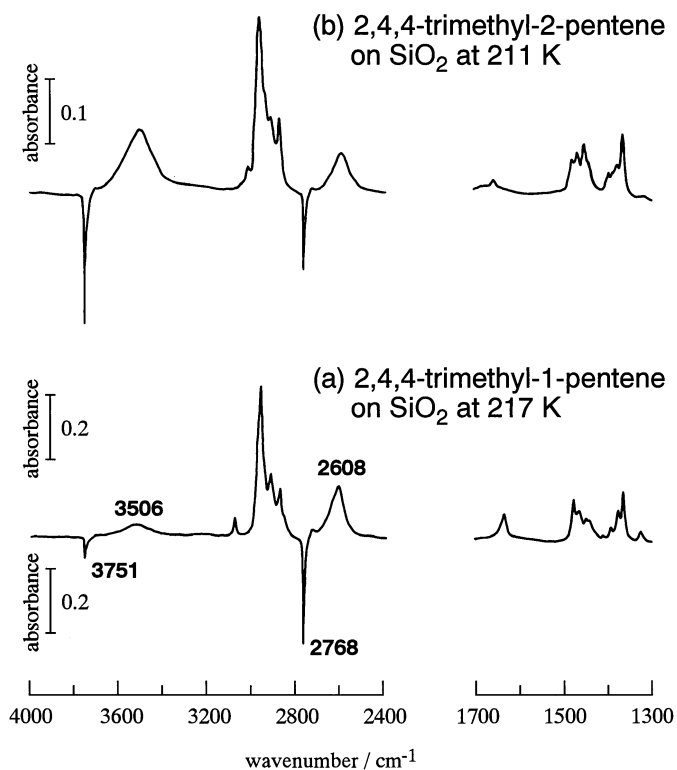


FIG. 5. Adsorption of (a) 2,4,4-trimethyl-1-pentene at 217 K and (b) 2,4,4-trimethyl-2-pentene at 211 K.

adsorbed species formed from possible dimer compounds of isobutene, 2,4,4-trimethyl-1-pentane, and 2,4,4-trimethyl-2-pentene were studied. IR spectra of both  $C_8$ -olefins adsorbed on silica (Fig. 5) and ferrierite (Fig. 6) are compared. About  $2.0 \times 10^{-5}$  mol of each  $C_8$ -olefin was introduced into the IR cell below 150 K, followed by evacuation. Then the cell was gradually warmed under evacuation, while IR spectra were measured. Therefore, desorption or reactions of irreversibly adsorbed species were observed in the spectra during the course of the experiment. All the IR spectra of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene adsorbed on amorphous silica were the same at various temperatures below 250 K, and typical spectra of both species are shown in Fig. 5. They were reasonably assigned to the molecularly adsorbed species by comparison with the IR spectra of these species in the liquid phase (12). Olefinic CH stretching bands were isolated from other CH stretching bands and appeared above  $3000\text{ cm}^{-1}$ . Another feature that indicated olefinic character is the C=C stretching bands in the  $1600\text{--}1700\text{ cm}^{-1}$  region. In the  $1300\text{--}1400\text{ cm}^{-1}$  region, CH deformation bands of  $>C(CH_3)-$ ,  $-C(CH_3)_2-$ , and  $-C(CH_3)_3$  groups were observed, and CH deformation of  $>C(CH_3)-$ ,  $>CH-$  and  $-CH_2-$  groups appeared in the  $1400\text{--}1500\text{ cm}^{-1}$  region (7). The negative bands at  $3751$  and  $2768\text{ cm}^{-1}$  correspond to the free silanol groups, which were converted to hydrogen-bonded groups at  $3506$  and

$2608\text{ cm}^{-1}$ , respectively. Therefore, it was found that both  $C_8$ -olefins adsorbed onto silanol groups on amorphous silica via hydrogen-bonding at temperatures below 250 K. On the other hand, very different spectra were observed on ferrierite.

Figure 6 shows IR spectra of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene adsorbed on ferrierite at 219 K. Both of the adsorbed species resulted in the same spectra, and neither of them was assigned to the molecularly adsorbed species by comparison with the spectra in Fig. 5. The reaction was accompanied by the consumption of silanol groups, which was evidenced by the absence of any hydrogen-bonded OH band. Therefore, it is considered that a reaction of  $C_8$ -olefins already proceeded on silanol groups on ferrierite at 219 K while they maintained their molecular structure on amorphous silica in a similar temperature range. Because the olefinic character of both  $C_8$ -olefins (CH stretching band above  $3000\text{ cm}^{-1}$  and C=C stretching band in the  $1600\text{--}1700\text{ cm}^{-1}$  region) was lost after adsorption and reaction, and because the products after the reaction of the same  $C_8$ -olefins on the acidic OH groups were  $C_8$ -alkoxy groups (3, 4), the species formed were assumed to be also  $C_8$ -alkoxy groups. There exist alternatives for both  $C_8$ -olefins to form corresponding alkoxy groups, 2,4,4-trimethyl-1-pentoxy and 2,4,4-trimethyl-2-pentoxy groups for 2,4,4-trimethyl-1-pentene, and 2,4,4-trimethyl-2-pentoxy and 2,4,4-trimethyl-3-pentoxy groups

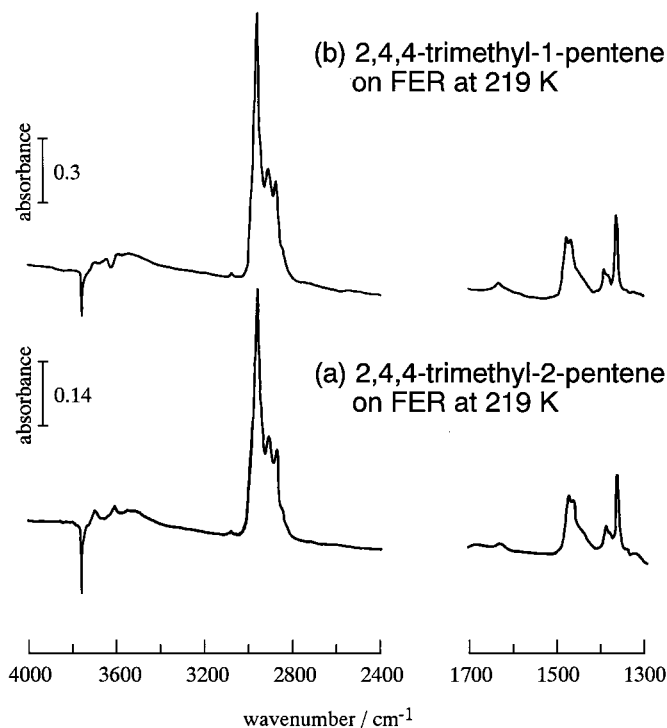
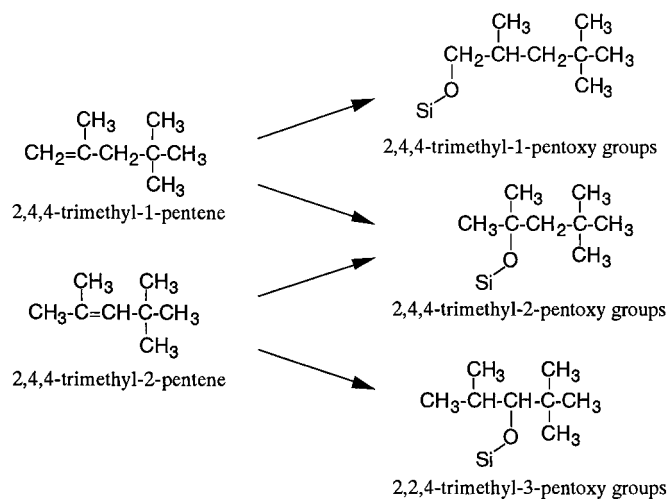


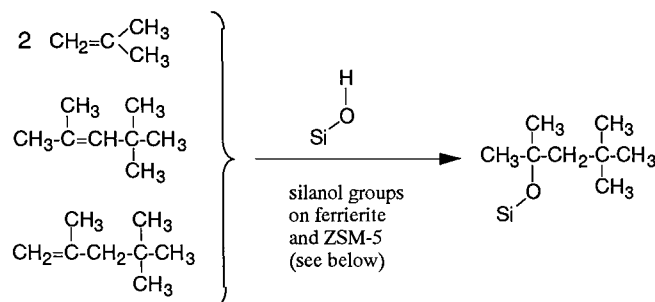
FIG. 6. Adsorption of (a) 2,4,4-trimethyl-2-pentene and (b) 2,4,4-trimethyl-1-pentene on ferrierite at 219 K.

for 2,2,4-trimethyl-2-pentene:



The fact that both  $\text{C}_8$ -olefins resulted in the same product indicates the formation of 2,4,4-trimethyl-2-pentoxy groups. Olefinic CH and C=C stretching bands are missing in IR spectra of 2,4,4-trimethyl-2-pentoxy groups. CH deformation bands of  $-\text{C}(\text{CH}_3)_2-$  and  $-\text{C}(\text{CH}_3)_3$  in the 1300- to 1400- $\text{cm}^{-1}$  region and those of  $>\text{C}(\text{CH}_3)-$  and  $-\text{CH}_2-$  groups in the 1400- to 1500- $\text{cm}^{-1}$  region (7) were simplified compared with those of the original  $\text{C}_8$ -olefins, probably due to the whole paraffinic character losing the olefinic  $-\text{CH}=\text{C}(\text{CH}_3)_2$  or  $-\text{C}(\text{CH}_3)=\text{CH}_2$  groups.

It should be noted that both spectra in Fig. 6 are identical to those of the species observed in Figs. 4c and 4b, which is the reaction product of isobutene on silanol groups of ferrierite. Accordingly, it is concluded that isobutene adsorbed and reacted to form dimeric 2,4,4-trimethyl-2-pentoxy groups on silanol groups of ferrierite zeolite:



The reactivities of silanol groups on ferrierite and on amorphous silica with  $\text{C}_8$ -olefins were also found to be remarkably different. This evidences the higher reactivity of silanol groups on ferrierite than of those on amorphous silica, even if the  $\text{C}_8$ -alkoxy groups were formed from migration of  $\text{C}_8$ -olefins, which were produced from isobutene on different active sites.

#### Reactivity of Silanol Groups on H (D)-ZSM-5 with 2,4,4-Trimethyl-1-pentene and 2,4,4-Trimethyl-2-pentene

In our previous study of the dimerization of isobutene on the acidic OH groups on mordenite, Y, and ZSM-5 zeolites

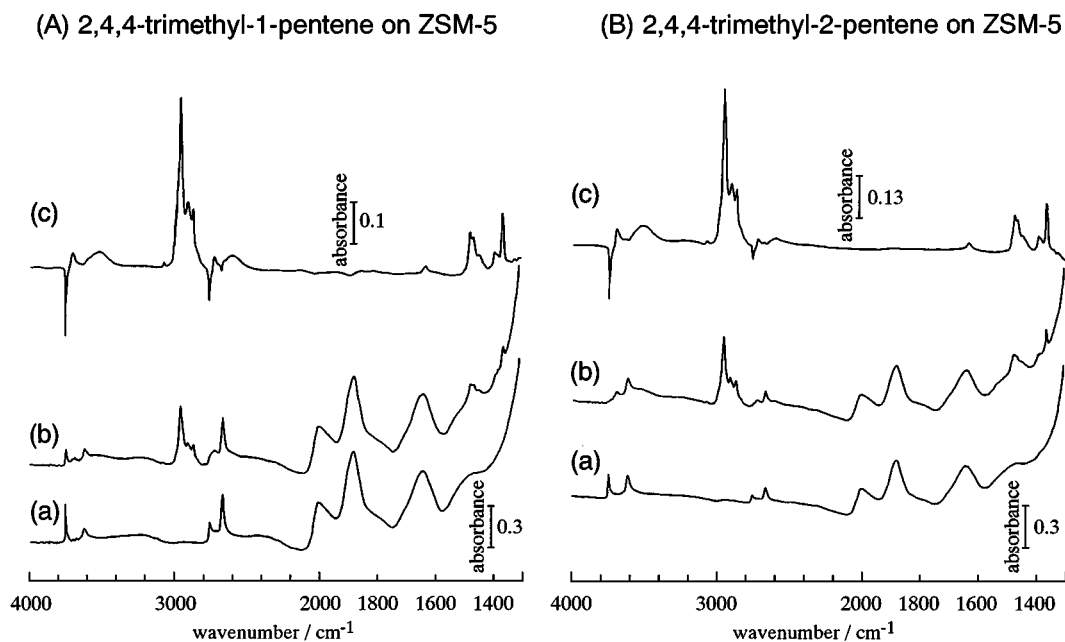


FIG. 7. Adsorption of (A) 2,4,4-trimethyl-1-pentene at 218 K and (B) 2,4,4-trimethyl-2-pentene at 219 K, both on ZSM-5. Spectra (a) and (b) were measured before and after adsorption, and (c) represents the difference spectrum.

and silica–alumina, simultaneous reaction of silanol groups also occurred (3, 4). Similarly to the case of ferrierite, the fact that the adsorbed 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene species could not access the acidic OH groups in small pores on ZSM-5 clearly demonstrated proton transfer to the C<sub>8</sub>-olefins from the silanol groups on the external surface. IR spectra of partially deuterated H (D)-ZSM-5 before and after adsorption of C<sub>8</sub>-olefins are shown in Figs. 7A and 7B for 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, respectively. In both cases, reduction of silanol groups was observed, while the acidic sites were unchanged in both the OH and OD stretching regions. The difference spectra shown in Figs. 7A-c and 7B-c are identical to those of 2,4,4-trimethyl-2-pentoxy groups, indicating that silanol groups on ZSM-5 are also more acidic than those on amorphous silica.

### SUMMARY

As shown above, the silanol groups existing on the external surface of zeolites, in general, could be concluded to be slightly more acidic than those on amorphous silica. The difference in acid strength of silanol groups is most probably attributed to the slight stress due to the inclusion of silanol groups in the highly crystallized structures of zeolites, although they exist on the external surface. This seems to account for the difference from the silanol groups on amorphous silica, which would stay in their most stable configurations.

### ACKNOWLEDGMENTS

This work was carried out as a research project of The Japan Petroleum Institute, commissioned by the Petroleum Energy Center with the support of the Ministry of International Trade and Industry.

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