

Stable Dimerized Alkoxy Species of 2-Methylpropene on Mordenite Zeolite Studied by FT-IR

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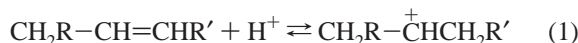
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Adsorption and reactions of 2-methylpropene (isobutene) on mordenite were investigated between 150 and 300 K by infrared (IR) spectroscopy. The methyl groups of isobutene interacted with the acidic OH groups of mordenite below 160 K, which was converted to the strongly interacted π -bonded isobutene to the acidic OH groups (π -complex). Above 200 K, the π -bonded isobutene dimerized even under evacuation condition. The stable 2,4,4-trimethyl-2-pentoxo species was identified by FT-IR by comparison with the spectra of the adsorbed C₃ olefins. The expected monomeric reaction intermediate, the 2-methyl-2-propoxy (*tert*-butoxy) species, was not observed. This is probably due to the rapid migration and reaction of the adsorbed isobutene molecules.

1. Introduction

Catalytic reactions utilizing solid acids, represented by a class of zeolites, are now indispensable for industrial chemistry. Zeolites are regarded as one of the most attractive materials as catalysts. The acidity of zeolites is classified into Brønsted and Lewis acid sites. Brønsted acid sites exist as bridging OH groups to Al and Si atoms, whereas Lewis acid sites are generated by elimination of Brønsted acid sites from zeolites or attributed to Al sites in extra frameworks. The skeletal and the open structures¹ of the mordenite zeolite used in this study are illustrated in Figure 1.

In solution chemistry, the reaction of an olefin with a Brønsted acid is generally known to form a carbenium ion, e.g.



The carbenium ions are regarded as important intermediates for many acid-catalyzed reactions.^{2,3} The importance of the protonated intermediates and the mechanism are also emphasized for catalysis of solid acids.^{4,5} Although the reaction mechanisms on the acidic OH groups of zeolites are regarded as in the same analogy as those established in solution chemistry,⁶ some unique natures of Brønsted acid sites on zeolites and some differences of them from protons in solvents have recently been demonstrated by the quantum chemical calculations,^{7–9} NMR¹⁰ and IR.^{11,12} In light of reactions of olefins and Brønsted acid sites, several alkoxy species were detected as products by NMR studies on HY and H-ZSM-5 zeolites,¹⁰ similar to those from reactions of alcohols.^{13–15} On the other hand, most of the IR studies have focused on the formation of carbenium type species starting from alcohol adsorption on zeolites.^{16–18} IR studies of olefin adsorption on H-form zeolites very often result in observation of oligomerization and polymerization product due to the rapid reaction

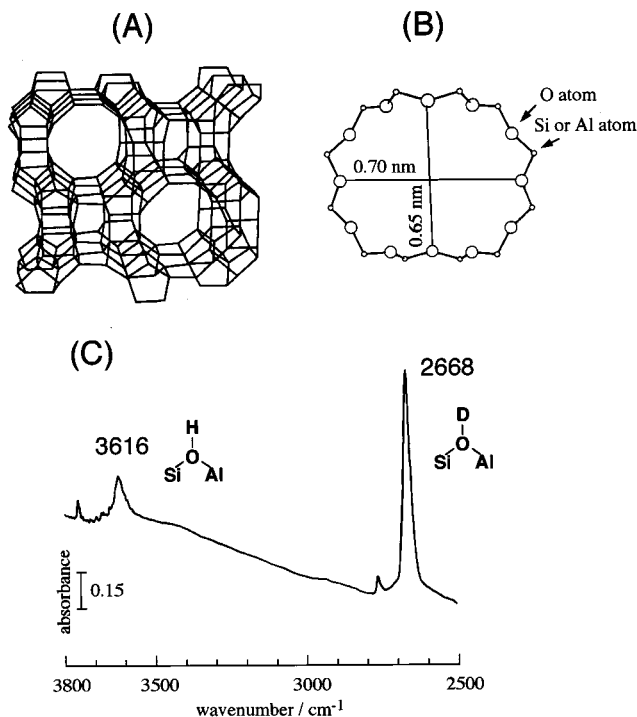


Figure 1. Skeletal diagram (A), open aperture of 12-membered ring along the [001] direction (main channel) (B), and IR spectrum of deuterated mordenite zeolite (C).

after proton transfer from Brønsted acid sites to the adsorbed olefins.^{19,20} A recent IR study of 2-methylpropene (isobutene) adsorption on H-ZSM-5 showed the formation of 2-methyl-2-propoxy (*tert*-butoxy) species below room temperature, where oligomerization simultaneously proceeded.²¹ On the other hand, the stable species of isobutene adsorbed on zeolites below 200 K were suggested as the dimer species by solid-state NMR.²²

We have been studying the reactions of *n*-olefins, which initiate with the π -bonded precursors. In the case of *n*-butene, double bond migration of 1-butene was independently observed

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from the two concurrent reactions, *cis/trans* isomerization and H/D isotope exchange, although no stable intermediates such as alkoxy groups were detected.^{11,12} It was also found that at the reaction temperatures of *cis/trans* isomerization and H/D isotope exchange, the adsorbed butene molecules were mobile, leading to dimerization.^{23,24} Herein, we report the reactions of isobutene whose monomeric intermediate, *tert*-butoxy species, is expected to be more stable than those of *n*-butene. Behavior of the adsorbed species and the structure of stable alkoxy groups are discussed.

2. Experimental Section

Sample Preparation. Mordenite zeolite, JRC-Z-HM20 with a ratio of Si/Al = 10, was provided by the Catalysis Society of Japan. The sample was pressed to the self-supporting IR disks (20 mm diameter, 40–50 mg) and was placed in an IR cell, which was attached to a conventional closed-circulation glass system. The pretreatment of the sample was conducted by circulating O₂ (100 Torr, 1 Torr = 133.322 Pa) at 773 K with a liquid nitrogen trap for 1.5 h and evacuation (10^{−3} Torr) at the same temperature for 15 min in order to remove residual contaminants. Then, the sample was treated with circulating H₂ (100 Torr) at 673 K for 1 h followed by evacuation during the cooling procedure to the low temperatures. Deuteration of H-mordenite was conducted in a similar manner with D₂. A typical IR spectrum of deuterated (D-) mordenite measured in evacuation is shown in Figure 1c. Although zeolites are well-known to have Brønsted and Lewis acid sites, the pretreatment condition was chosen to produce no Lewis acid sites on mordenite, and the absence of them was confirmed by using CO molecules as a probe.²⁵

Reagents. Isobutene (Takachiho Trading Co., Ltd., 99.0% purity) was purified by vacuum distillation and freeze–pump–thaw cycles. D₂ (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), 2,4,4-trimethyl-2-pentene (99% purity), and 2,4,4-trimethyl-1-pentanol (98% purity) were purchased from Aldrich Chemical Co., Inc., and also purified by vacuum distillation and freeze–pump–thaw cycles before use.

IR Measurements. The IR spectra were obtained by a JASCO 7300 FT-IR spectrometer equipped with a 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 in evacuation at various temperatures, and they were used as background spectra. Subtracted IR spectra of the background spectra from those with adsorbed species are shown in this paper. The temperature which was monitored by a thermocouple attached near the sample was controlled by cooling with liquid nitrogen flow and electrical heating. The temperature monitored by thermocouple attached to the IR cell was calibrated to the real temperature of the sample disk. The quantity of olefin introduced onto the sample was controlled to less than 10% of that of the Brønsted acid sites, and the IR cell was immediately evacuated, so that intermolecular interaction was restricted.

3. Results and Discussion

IR Spectra of Isobutene Adsorbed on Mordenite. IR spectra of isobutene adsorbed onto D-mordenite are shown in Figure 2. Deuterated mordenite was used to separately observe the hydrogen-bonded hydroxyl bands and CH stretching bands of adsorbate. Isobutene (23.5 μmol) was at first introduced at 140 K, and the sample was gradually warmed under evacuation.

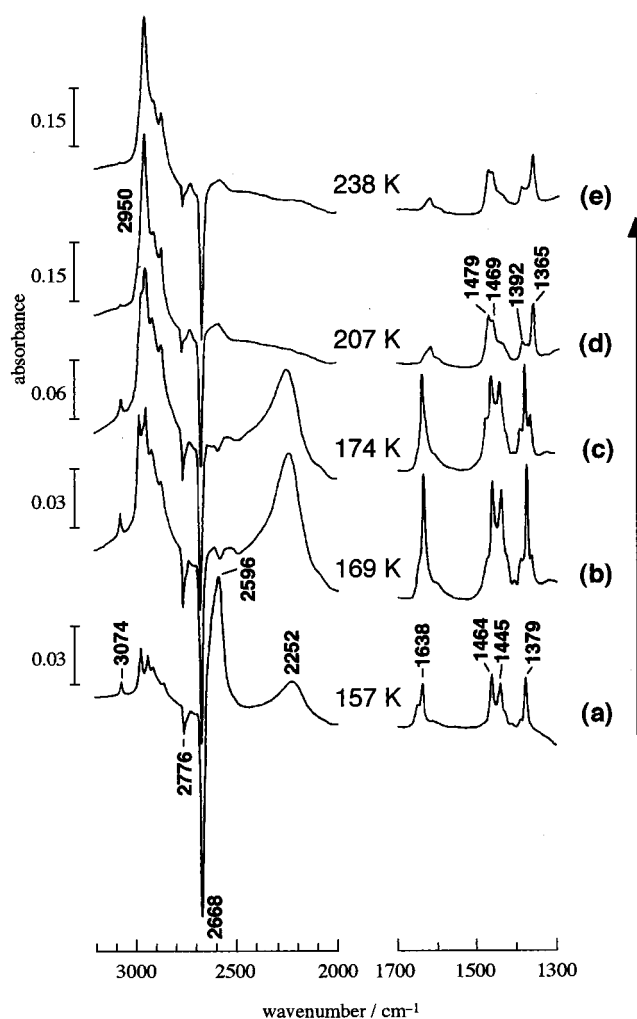


Figure 2. FT-IR spectra of isobutene adsorbed on mordenite under evacuation at 238 K (a), 207 K (b), 174 K (c), 169 K (d), and 157 K (e). Isobutene (23.5 μmol) was introduced at 140 K and gradually warmed under vacuum.

In Figure 2a, the bands at 1379, 1445, and 1464 cm^{−1} are assigned to the CH bending ($\delta(\text{CH})$) modes and that at 1638 cm^{−1} is to the C=C stretching ($\nu(\text{C}=\text{C})$) mode of isobutene. Some peaks at around 3000 cm^{−1} are assigned to CH stretching ($\nu(\text{CH})$) mode, particularly, the band at 3074 cm^{−1} is attributed to the olefinic $\nu(\text{=CH}_2)$ mode. These peaks are identical to isobutene molecules, which appeared in the IR spectrum of isobutene in gas, liquid, and solid phases²⁶ as well as that adsorbed on SiO₂.²⁷ The negative peaks at 2776 and 2668 cm^{−1} due to OD stretching ($\nu(\text{OD})$) bands of silanol and the Brønsted acid sites of D-mordenite, respectively, were observed because of the decrease of the isolated OD species by interaction of the adsorbed isobutene. Alternatively, two broad $\nu(\text{OD})$ bands appeared at 2596 and 2252 cm^{−1}. The former $\nu(\text{OD})$ band is partly attributed to the hydrogen-bonded silanol to C=C bond of isobutene (evidenced by an IR spectrum of isobutene adsorbed on deuterated SiO₂ at similar temperature). However, contribution of the hydrogen-bonded silanol to the band at 2596 cm^{−1} would be small judging from the weak negative band of silanol at 2776 cm^{−1}. The small downward shift of the acidic OD band to the former ($-\Delta = 72 \text{ cm}^{-1}$) is a result of the weak hydrogen-bonding interaction between the methyl groups of isobutene and the acidic OD groups. This was further confirmed by adsorption of ethane. The same weakly hydrogen-bonded OD band was observed when ethane was adsorbed on D-

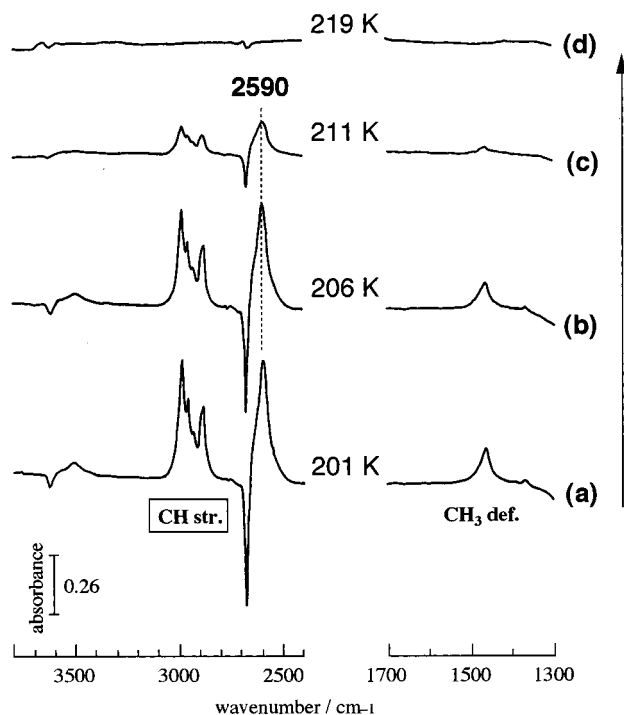
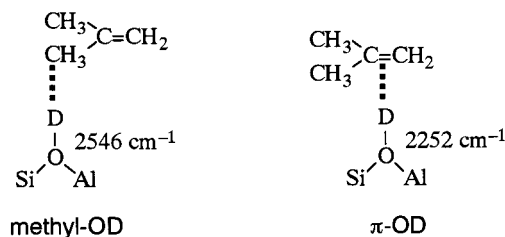


Figure 3. IR spectra of ethane adsorbed on mordenite under evacuation at 219 K (a), 211 K (b), 206 K (c), and 201 K (d). Ethane (54.0 μ mol) was introduced at 150 K and gradually warmed under vacuum.

mordenite at 150 K followed by evacuation below 220 K as shown in Figure 3. Ethane is supposed to have interaction with the acidic OD groups via the methyl groups. The ν (OD) band at 2252 cm^{-1} is attributed to the 1:1 π -complex showing a large red shift ($-\Delta = 416 \text{ cm}^{-1}$), and increased due to the conversion from weakly hydrogen-bonded species by increasing the temperature in evacuation to 169 K (spectrum b in Figure 2).²⁸ The structures of the hydrogen-bonded species to OD groups with the methyl groups and the π -bond of isobutene (methyl-OD and π -OD complexes) are depicted as follows.

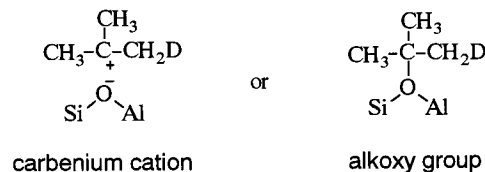


Simultaneously with the thermal conversion from the methyl-OD to the π -OD hydrogen-bonding, changes in IR spectra were observed in Figures 2a–c; the intensity of the paraffinic ν (CH) bands became larger compared with that of the olefinic one, and two peaks appeared at both shoulders of the band at 1379 cm^{-1} . These spectral changes became evident by further increase in temperature above 200 K. At 207 K, the hydrogen-bonded OD band (π -OD) was completely consumed. The hydrogen-bonded OD groups were not reversibly converted to the isolated ones, since the negative band of the isolated OD groups still remains in Figure 2d. Concurrently, the olefinic ν (CH) and the ν (C=C) bands characteristic to isobutene disappeared, and δ -(CH) vibrations (1500–1300 cm^{-1}) appeared differently. It is, therefore, considered that a reaction of the π -complex (adsorbed isobutene and the acidic OD groups) occurred, and the spectrum in Figure 2d is assigned to the reaction product of the 1:1 π -complex of the acidic OD groups and isobutene molecules.

The reaction product is regarded as considerably stable to 238 K, which is discussed below.

It is also interesting to mention that the silanol OD peak appeared as a negative one in the whole spectra of Figure 2. In the as-observed spectra, OD bands of silanol groups definitely were consumed. This may indicate the participation of the silanol groups of zeolites to the reaction of isobutene in contrast to silanol groups on amorphous silica. Details will be shown elsewhere.

Assignment of the Reaction Product from Isobutene. Identification of the reaction product of isobutene and the acidic OD groups on mordenite was attempted. At first, we considered that this product would be either tertiary carbenium cations or alkoxy group, which are illustrated as follows.



The spectrum of the $(\text{CH}_3)_3\text{C}^+$ cation in SbF_5 solvent showed a broad ν (CH) band at lower frequency region (centered 2830 cm^{-1}), and δ (CH) bands appeared considerably weaker than the ν (CH) band.²⁹ A comparison of the IR spectrum of $(\text{CH}_3)_3\text{C}^+$ cation with that of the reaction product of isobutene and the acidic OD groups showed no similarities in the spectral appearance in both ν (CH) and δ (CH) regions. This excluded the assignment of that to the tertiary carbenium cations. The possibility of formation of the tertiary alkoxy groups was then considered.

Figure 4 compares the IR spectra of (a) the reaction product of isobutene on mordenite, (b) the species formed by adsorption of *tert*-butanol on mordenite, and (c) 2-methyl-2-propoxy (*tert*-butoxy) group formed by *tert*-butanol adsorption on ZrO_2 . It is known that alkoxy groups are produced by adsorption of alcohols on the ZrO_2 surface followed by evacuation above 373 K.³⁰ The formation of *tert*-butoxy species on ZrO_2 was confirmed by the existence of the ν (C–O) band at 1036 cm^{-1} due to alkoxy groups, which appeared at largely different frequency from that of *tert*-butanol (1114 cm^{-1}).³¹ The spectrum (b) was recorded after adsorption of *tert*-butanol on mordenite and immediate evacuation at 253 K. The adsorbed species were expected to be either butanol or deprotonated butoxy groups formed by dehydration on acid sites. Adsorption of *tert*-butanol on mordenite above 253 K or after leaving at 253 K for more than 10 min resulted in large changes in spectral appearance even in evacuation due to acid-catalyzed reactions of the alcohol. These two spectra (b) and (c) were used as references of *tert*-butoxy groups ($-\text{O}-\text{C}(\text{CH}_3)_3$) for comparison. While three bands were observed in 3000–2800 cm^{-1} region in spectrum (a) of the reaction product of isobutene, four ν (CH) bands were resolved in spectra (b) and (c). In the δ (CH) region, asymmetric bands (1300–1400 cm^{-1}) appeared much more intensively than the symmetric ones (1400–1500 cm^{-1}) for *tert*-butoxy groups,³² as was also observed in this study (spectra (b) and (c)). On the other hand, bands in these two modes were equally observed in intensity for the isobutene-derived species. These differences led us to consider possibilities of the assignment of the reaction product of isobutene other than *tert*-butoxy groups, although isobutene is proposed to be stabilized as *tert*-butoxy species on zeolite by chemical calculations.^{7,8} It is mentioned that the possibility of the formation of 2-methyl-1-propoxy (isobutoxy) groups was excluded by comparison of the spectrum with that

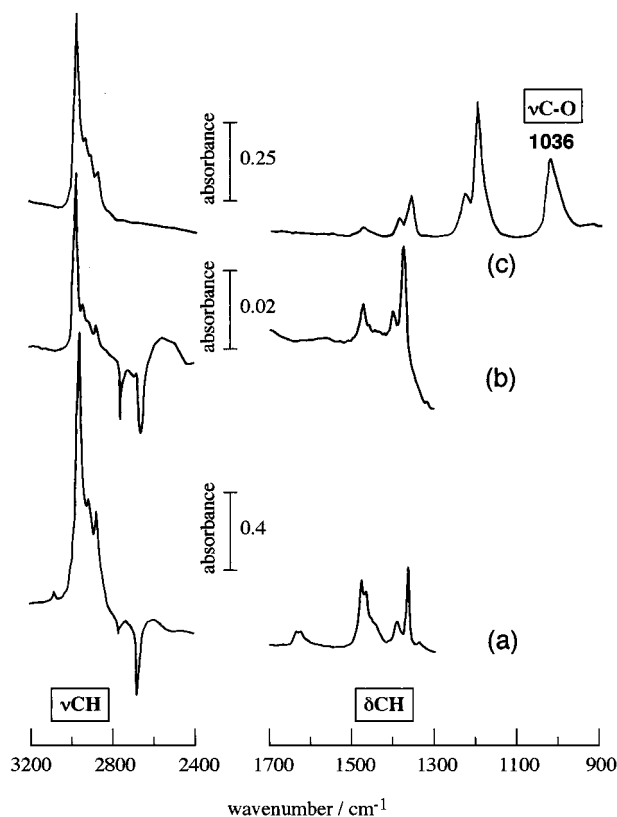


Figure 4. IR spectra of (a) the reaction product of isobutene on D-mordenite (Figure 2d), (b) *tert*-butanol adsorbed on deuterated mordenite followed by evacuation at 253 K, and (c) *tert*-butoxy group produced by *tert*-butanol adsorption on ZrO_2 . *tert*-Butanol (284 μmol) was exposed on ZrO_2 at room temperature and gradually warmed under evacuation. Spectrum (c) was measured at 398 K.

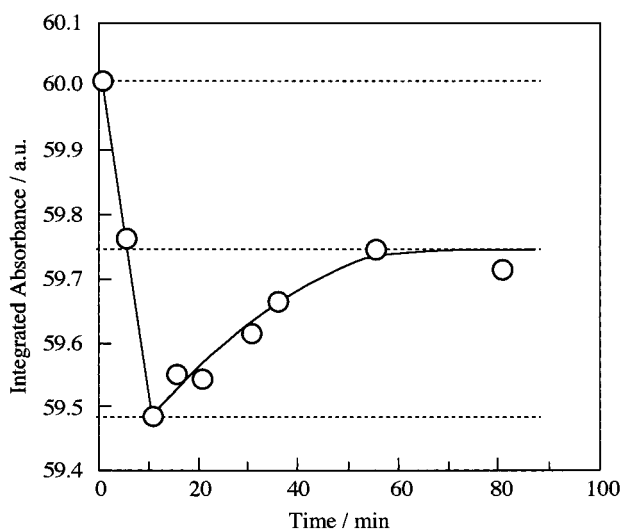
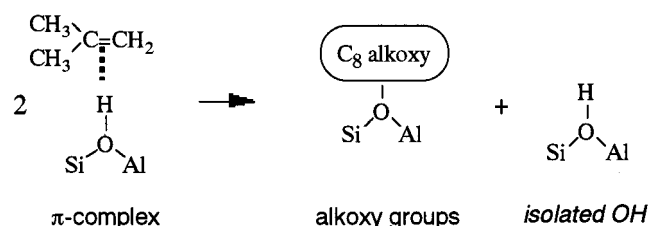


Figure 5. The time course of the integrated absorbance of the band of the isolated Brønsted acid sites after isobutene introduction on mordenite at 170 K followed by evacuation at the same temperature.

of isobutoxy groups formed from adsorption of 2-methyl-1-propanol (isobutanol) onto ZrO_2 followed by evacuation (not shown).

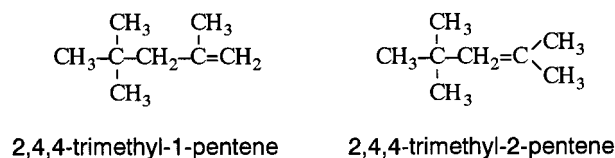
It was found in our previous study that *n*-butene was stabilized as dimer species²⁴ and that adsorbed *n*-butene migrated well below room temperature on zeolite.²³ Therefore, we counted the production of dimer or oligomer as a result of the reaction, although the reaction temperature was relatively low with the limited amount of adsorbed species (less than 10% of the acid

sites). The following experiment was quantitatively analyzed. Isobutene was introduced on H-mordenite at 170 K followed by evacuation. H-mordenite was used in place of D-mordenite in order to exclude the influence of the isotope exchange reaction on the change of isolated OH (OD) groups. The time course of the integrated intensity of isolated Brønsted acidic OH groups was measured as shown Figure 5. In the initial 10 min, the isolated acidic OH groups decreased due to adsorption to about 1% of the acidic OH groups, forming π -OH complexes. After 10 min, gradual recovery of the amount of the isolated OH groups was observed, which finally reached to about a half of the initial consumption as indicated by dotted lines. This indicates that the dimer was produced from π -interacted isobutene molecules on H-mordenite; a half of the peak intensity of the isolated OH band regained because of the regeneration of the vacant Brønsted acid sites accompanied with the dimerization of the adsorbed isobutene.



In the above scheme, the product is assigned as alkoxy groups, details of which are shown below. The fact that dimerization occurred at such a low occupation of the acidic OH groups by isobutene indicates that the observed π -complex between isobutene and the acidic OH groups did not statically exist but was observed in equilibrium with rapidly migrating species even at 170 K. In Figure 2d, a new $\nu(\text{C}=\text{C})$ band at lower frequency than that of isobutene (Figure 2c) is probably attributed to the formed C_8 olefin as shown below.

Structure of the Dimer Species. The reaction product was supposed to be a dimer species by observation of the isolated OH groups in the previous section. Further confirmation of the assignment as well as the structure of the dimer species on the acid sites was examined by comparison of IR spectra. Assuming the olefin product, the dimerized isobutene is expected to be either 2,4,4-trimethyl-1-pentene or 2,4,4-trimethyl-2-pentene.



IR spectra of these C_8 olefins were measured by adsorption of them on deuterated SiO_2 at 140 K followed by evacuation. Spectra (a) and (b) in Figure 6 are due to the 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene on deuterated SiO_2 at 220 K in evacuation, respectively. The C_8 olefins are found to adsorb on OD groups by π -bonding (isolated OD band shifted to ca. 2600 cm^{-1}), and these spectra are identical to 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene in the liquid phase.³³ On the other hand, when the C_8 olefins adsorbed on D-mordenite in the same condition, they reacted with the acidic OD groups as seen in spectra (c) and (d); no hydrogen-bonded OD bands were observed but the acidic OD band was simply consumed, and the $\delta(\text{CH})$ region of the adsorbed species appeared differently from those of the olefins. The products are not regarded as cationic species from the same reason for

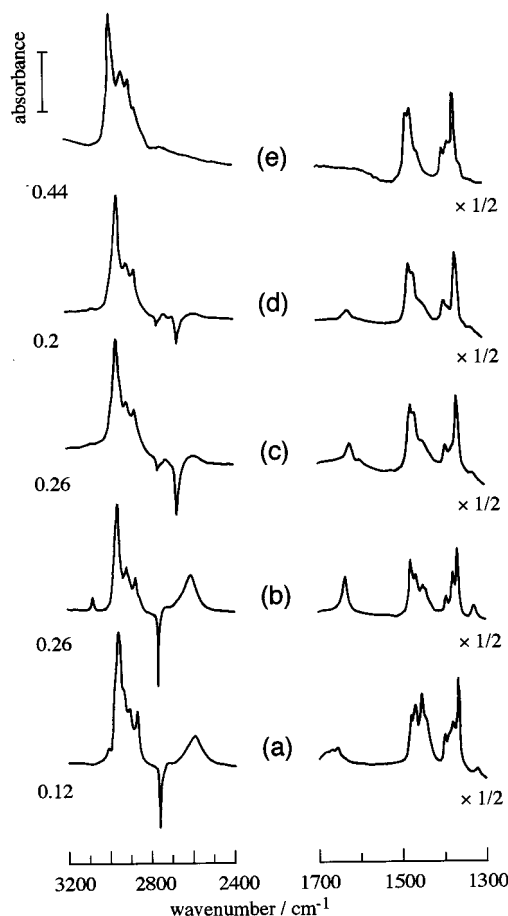
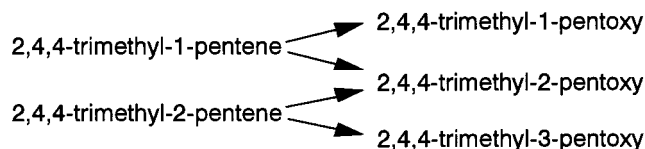


Figure 6. Comparison of IR spectra of the reaction product of isobutene with some C₈ olefins on mordenite and SiO₂: (a) 2,4,4-trimethyl-2-pentene adsorbed on SiO₂, (b) 2,4,4-trimethyl-1-pentene adsorption on SiO₂, (c) 2,4,4-trimethyl-2-pentene adsorbed on deuterated mordenite, (d) 2,4,4-trimethyl-1-pentene adsorbed on deuterated mordenite, and (e) IR spectrum of 2,4,4-trimethyl-1-pentoxo species formed by adsorption of 2,4,4-trimethyl-1-pentanol on ZrO₂. The alcohol (18.5 μ mol) was dosed at room temperature, and then the sample was gradually warmed under evacuation. The spectrum was measured at 398 K.

exclusion of *tert*-butyl cation (the absence of considerably intense and broad $\nu(\text{CH})$ band, see above), and the assignment to C₈ alkoxy species is then discussed.

A C₈ alcohol, 2,4,4-trimethyl-1-pentanol, was adsorbed on ZrO₂ to form 2,4,4-trimethyl-1-pentoxo groups similarly to the production of *tert*-butoxy groups. Although the IR spectrum of 2,4,4-trimethyl-2-pentoxo species could not be obtained due to impurities in the synthesized 2,4,4-trimethyl-1-pentanol, a spectrum of 2,4,4-trimethyl-1-pentoxo groups on ZrO₂ (Figure 6e) is compared with Figure 6d, 2,4,4-trimethyl-1-pentene-derived species on mordenite. These two spectra differ slightly in the $\delta(\text{CH})$ region; three bands are resolved in the symmetric modes (1300–1400 cm⁻¹) in spectrum (e), while the central band is not clear in (d); and in the asymmetric modes (1400–1500 cm⁻¹), intensities of two bands are seen in the opposite order. Therefore, it is suggested that the observed species formed by the reaction of 2,4,4-trimethyl-1-pentene on the acid sites are not 2,4,4-trimethyl-1-pentoxo groups. The other possible C₈ alkoxy species formed from the reaction of 2,4,4-trimethyl-1-pentene on the acid sites are 2,4,4-trimethyl-2-pentoxo groups.

Similarly to 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene has two possible structures for alkoxy groups after protonation from Brønsted acid sites. It must be mentioned here that the product of the two different C₈ olefins on the acidic



sites resulted in exactly the same IR spectra (c) and (d), i.e., the same species were formed. This fact clearly indicates the formation of 2,4,4-trimethyl-2-pentoxo species from the reaction of either 2,4,4-trimethyl-1-pentene or 2,4,4-trimethyl-2-pentene with the acidic OD groups. Although most of 2,4,4-trimethyl-1-pentene molecules are considered to become the alkoxy species, a small part of them remained as olefin (see weak $\nu(\text{C}=\text{C})$ band), whose contribution to the whole spectrum is not apparent. The most important conclusion is derived by comparison of IR spectra of 2,4,4-trimethyl-2-pentoxo groups with that of the reaction product of isobutene (Figure 2d or 3a): the reaction product of isobutene on mordenite is considered to be equivalent to the 2,4,4-trimethyl-2-pentoxo species. It is also noticed that a small amount of olefin molecules observed in Figure 6c, which started with 2,4,4-trimethyl-2-pentene, shows the $\nu(\text{C}=\text{C})$ band due to 2,4,4-trimethyl-1-pentene. Therefore, both C₈ olefins as well as isobutene are found to form 2,4,4-trimethyl-2-pentoxo groups and a small amount of 2,4,4-trimethyl-1-pentene as a result of reactions with the acidic OD groups in the cage of mordenite.

The Reactivity of the Alkoxy Species on Mordenite. Next, the reactivity of the dimer alkoxy species formed from isobutene reaction was studied. The 2,4,4-trimethyl-2-pentoxo-covered D-mordenite (about 30% occupation of the total number of Brønsted acid sites) was then reexposed to isobutene in the same manner and at the same temperature. Temperature was kept constant for this experiment. The dosed isobutene molecules have two possible reaction routes; either reaction with surface 2,4,4-trimethyl-2-pentoxo groups or adsorption on vacant Brønsted acid sites. If 2,4,4-trimethyl-2-pentoxo groups are highly reactive for oligomerization, the former reaction would dominantly proceed. However, additional 2,4,4-trimethyl-2-pentoxo species formation from the reaction of supplied isobutene on unoccupied Brønsted acid sites was observed. Next, C₂D₄ was supplied from gas phase onto 2,4,4-trimethyl-2-pentoxo-covered D-mordenite at 188 K (about 90% occupation at 188 K). The temperature was then increased to 313 K in the presence of gaseous C₂D₄. No reactions between 2,4,4-trimethyl-2-pentoxo species and C₂D₄ proceeded, but reactions, decomposition and decrease of 2,4,4-trimethyl-2-pentoxo species due to the temperature increase, and adsorption and oligomerization of C₂D₄ on vacant sites, were independently observed. These results indicate that the tertiary 2,4,4-trimethyl-2-pentoxo groups were considerably stabilized and were not reactive under the present experimental conditions.

The Absence of Stable *tert*-Butoxy Species. The theoretical studies propose that the stable intermediates of the reaction of isobutene and Brønsted acid site are *tert*-butoxy species,^{7,8} which initially made us expect to observe them. However, dimerization rapidly occurred in practice, without forming any monomeric alkoxy species. This discrepancy would arise from the unexpectedly rapid migration of adsorbed isobutene molecules to the greatest extent above 200 K. When protons on Brønsted acid sites are transferred to the π -bonded isobutene, they are attacked by other molecules, resulting in dimerization even at less than 10% of coverage. It is therefore also concluded that the observed π -bonded isobutene molecules exist in equilibrium with migrating species in the cages of mordenite.

4. Conclusion

Adsorption and reaction of isobutene on D-mordenite were observed by IR spectroscopy. Two adsorption structures were found below 200 K depending on the sample temperature, methyl-OD and π -OD adsorptions, the former converted to the latter above 160 K. Above 200 K, the reaction of the π -bonded isobutene and the acidic OD groups was observed. The observed reaction product was assigned to the dimer 2,4,4-trimethyl-2-pentoxo species, which was very stable up to 300 K. The small energy barrier for migration of isobutene was regarded as the cause of the rapid dimerization without forming any stable monomeric *tert*-butoxy groups.

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