



IR observation of adsorption and reactions of olefins on H-form zeolites

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Abstract

Details of adsorption of olefin molecules in the micropores of zeolites are revealed by using low-temperature IR spectroscopy. The well-known π -adsorption of olefins was found to be an activation process from the weaker adsorption with alkyl–acidic OH (OD) interaction, which was in equilibrium with the adsorption on the internal wall. The energy diagram of such various adsorptions were found to be governed by the pore size, radius of curvature, of zeolites. The double bond shift of 1-butene to 2-butene was observed below 230 K on ZSM-5 and mordenite (MOR) as a result of intramolecular reaction, where the protons on the acidic OH groups were not involved in the reactant (2-butene). The initial intermolecular reaction of the formed 2-butene as well as isobutene terminated once at dimerization, and further reactions did not occur at room temperature, differently from the case of ethane and propene. Further studies, which are presently proceeding, and the prospective are also mentioned.

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1. Introduction

In addition to the practical importance of zeolites [1,2], their rigid microporous crystal structures [3] and the well-identified atomic structures of the active sites [4] motivate the fundamental researches on the catalysis of zeolites [5], a representative family of solid acids. The active sites of zeolites locate inside of their micropores, and are classified into Brønsted and Lewis acid sites. The Brønsted acidity is originated from the OH groups bridging to Si and Al, while the Lewis acid sites are generated from dehydration of Brønsted acid sites. The acidic OH (OD) groups can be directly observed by IR method as well as by

NMR spectroscopy. In IR studies, pyridine adsorption is regarded as a most frequently used manner, which distinguishes the presence and/or absence of Brønsted and Lewis acid sites [6,7]. On the other hand, CO and N₂ adsorption have been recently used to probe the really strong acidic sites [8,9]. CD₃CN is count as a probe of acidic sites [10], while halogenated methanes recently reported as a good probe of basic sites existing on zeolites [11]. However, studies of surface nature of zeolites using those probes do not directly give any information on the real catalysis, therefore, they stay within the limit of characterization. The most suitable probe molecules are suggested to be the reactants themselves [7]. Therefore, the detailed information on the adsorption, migration and reaction of hydrocarbon molecules can be regarded as the most useful knowledge to understand the catalysis of zeolites. Here, emphasis is put on how IR technique is

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powerful to examine the details on the behavior of hydrocarbon species on zeolites with such examples as adsorption and intramolecular as well as intermolecular reactions of olefins.

2. Experimental

In this study, ZSM-5 (Si/Al = 50; Sumitomo Chemical Co. Ltd.), ferrierite (FER) ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 17.0$; Tosoh Corp.) and mordenite (MOR) HM-20 (Si/Al = 10; Catalysis Society of Japan) are used in hydrogen forms. IR spectra of amorphous silica were also used to obtain reference spectra of adsorbed species on neutral OH groups. A thin disk of each zeolite (ca. 15 mg in 20 mm diameter) was placed in an IR cell connected to a closed gas-circulation system. Temperature of the sample was controlled from 100 to above 1000 K using this cell. Pretreatment of the samples was conducted first with O_2 at 773 K, followed by evacuation. Then a clean IR disk was further treated with D_2 at 673 K to switch OH groups to OD. This pretreatment condition produces no Lewis acid sites, which was confirmed by adsorption of probe molecules.

3. Results and discussion

3.1. IR spectra of H (or D)-form zeolites and observation of adsorbed olefins

IR spectra measured of the used zeolites after pretreatment are compared in Fig. 1 together with those of silica and silica–alumina. The OH and OD groups on silica appear at 3752 and 2765 cm^{-1} , respectively, which are almost the same as those on silica–alumina. In the case of silica–alumina, Brønsted acidity is attributed to the observed OH or OD species [12], although those on silica observed at the same frequencies only behave as neutral OH and OD groups. Therefore, the observed peak positions themselves are found not to be simply related to the acid strength for amorphous materials. On the other hand, the acidic OH and OD groups bridging to silicon and aluminum atoms in rigid crystal structures of zeolites are observed evidently at lower frequencies (ca. 3610 and 2665 cm^{-1} , respectively) than those of OH and OD groups on silica and silica–alumina as demonstrated

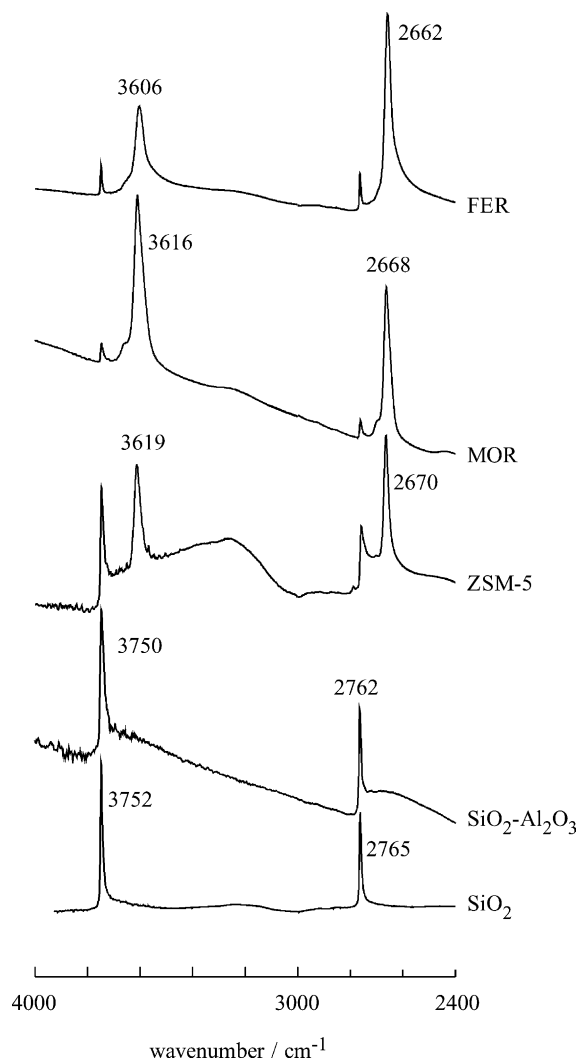


Fig. 1. IR spectra of deuterated silica, silica–alumina, ZSM-5, mordenite and ferrierite. Spectra were measured under evacuation at around 200 K after pretreatment.

in three upper spectra in Fig. 1. One of examples of the relation between the crystallized porous structure and the atomic structure of acid site is shown in Fig. 2. The pore structure is demonstrated in Fig. 2A, where each stick represents a Si–O–Si bond in the case of silicate. The detailed atomic structure is highlighted in Fig. 2B, which possesses an acidic OH groups due to substitution of one silicon atom to aluminum. The structure of a single Brønsted acid site is simply illustrated in Fig. 2C. Although the acidic nature and

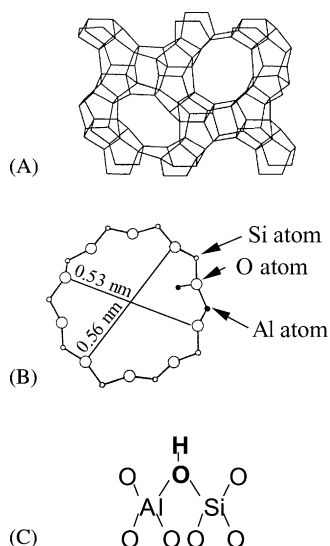


Fig. 2. The skeletal diagram (A) and the open apertures (B) of ZSM-5 and schematic description of Brønsted acid site (C). (A) In the skeletal structure, each straight line consists of either Si or Al atoms at the both ends and an O atom or an OH group in the middle. (B) The small and big open circles represent O atoms and Si atoms, while a closed small circle indicates an Al atom in the ring structure. A bridging OH group between Si and Al is also shown.

catalysis of zeolites are not thoroughly attributed to the local structure, such atomic structure is used in this study for simplicity.

The spectrum in Fig. 3A is D-ZSM-5 just after pretreatment, where more than 90% of the acidic OH groups are converted to OD ones. The acidic OD groups in the micropores of ZSM-5 show a band at 2671 cm^{-1} , whereas silanol groups existing on the external surface appear at 2761 cm^{-1} in Fig. 3A. The spectrum in Fig. 3B was measured after adsorption of ethene followed by evacuation at around 200 K. The decrease of the acidic OD band, and the appearance of some new bands are observed as marked with stars. However, details of the spectral change from before to after adsorption of ethane are not clear. Therefore, subtracted spectra are usually shown in this study, one of the examples of which is demonstrated in the spectrum C in Fig. 3, where the spectrum A, a background, was subtracted from the spectrum B. The acidic OD band appeared as a negative band due to the conversion from the isolated to the hydrogen-bonded species, which appears at 2380 cm^{-1} . All the other upward

bands in Fig. 3C are attributed to ethene adsorbed with its C=C bond onto the acidic OD groups as illustrated in the inset. As a result, the C=C stretching of ethane, which is originally IR inactive, becomes observable at 1612 cm^{-1} , shifting to lower frequency side from the Raman band (1623 cm^{-1}) of gas molecules [13].

3.2. Adsorption of 1-butene on D-ZSM-5

Olefin molecules are known to be stabilized on the acidic OH or OD groups of zeolites by forming π -complex. Ethene, propene and 1-butene also form the π -complexes with the acidic OD groups at around 200 K. The bands appearing at $1600\text{--}1700\text{ cm}^{-1}$ in all spectra in Fig. 4 are attributed to C=C stretching. The numbers in parenthesis indicate the amounts of shifts from the values of free molecules [14]. It is evident that all the C=C stretching bands shifted to lower frequencies, indicating the direct involvement of C=C bonds of olefins in adsorption. Especially in the case of ethene, the C=C stretching band becomes active upon adsorption as mentioned previously. The shifts of C=C bands in Fig. 4 are in coincidence with the shift of OD band from the position of the isolated to the hydrogen-bonded frequency. These π -complexes were the only adsorption structures of olefins on zeolites, observed so far. However, other types of adsorption are found if one goes to much lower temperature region.

Fig. 5 demonstrates the gradual change of IR spectra of adsorbed 1-butene during warming procedure at a heating rate of ca. 6 K min^{-1} under evacuation. 1-Butene was introduced to ZSM-5 below 150 K followed by evacuation. Then temperature was increased in evacuation, while measuring IR spectra. At 155 K (bottom spectrum in Fig. 5) the olefinic CH stretching band at 3080 cm^{-1} and C=C stretching band at 1640 cm^{-1} , which are identical to free 1-butene in Ar matrix [14] were observed. The acidic OD groups were found to interact with the adsorbed molecules from their negative peak at 2671 cm^{-1} , but the hydrogen-bonded OD band appeared at 2689 cm^{-1} with less shift compared with that in π -complexes (Fig. 4c). It is recalled that C=C stretching band of 1-butene stayed at the same frequency as that of free molecules in the same spectrum. Therefore, 1-butene is considered to adsorb onto the acidic OD groups with weak interaction regardless of participation of C=C bond. This type of adsorption was stable up to 166 K,

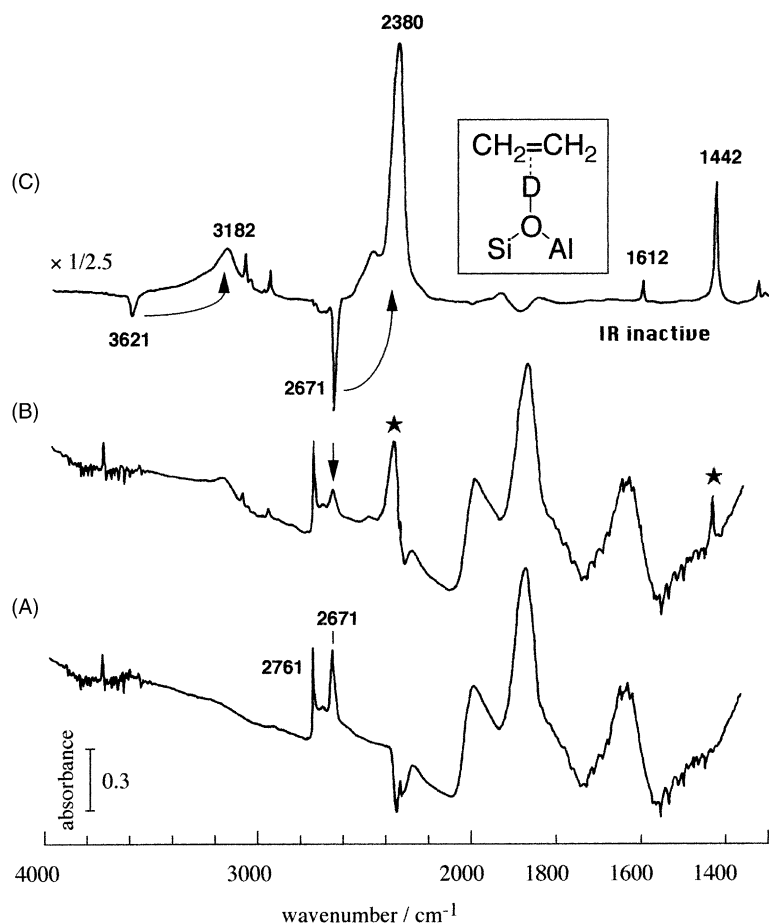


Fig. 3. IR spectra of D-ZSM-5 before (A) and after (B) adsorption of ethene at around 200 K. Spectrum (C) was obtained by subtraction of spectrum of (A) from that of (B).

then another type of adsorption, which has no relation to the OD groups was observed at 173 K. (See the disappearance of the negative band at 2671 cm^{-1} .) The new type of adsorption on the acidic OD groups below 170 K was assigned to the alkyl-OD interaction, which was confirmed by ethane adsorption. When ethane adsorbed on the acidic OD group, the OD band shifted to 2590 cm^{-1} . The amount of the shift is comparable with that with 1-butene adsorbed at 166 K. Therefore, 1-butene was found to adsorb on the acidic OD groups with alkyl-OD interaction, which is much weaker than π -OD interaction, because the amount of shift reflects the strength of interaction.

When temperature was increased to 173 K, the hydrogen-bonded OD band in alkyl-OD complexes

disappeared, while 1-butene molecules still adsorbed on ZSM-5. Since inside of the pores of ZSM-5 was found to be accessible from the presence of alkyl-OD complexes, 1-butene molecules are considered to adsorb on the wall of the cage of ZSM-5. It is mentioned that C=C bond of 1-butene has no relation to the adsorption on the wall, judging from the absence of any shift of C=C vibration.

The energy diagram and a sketch of 1-butene adsorption inside the pores of ZSM-5 are schematically demonstrated in Fig. 6. The alkyl-OD complex was observed at the lowest temperature range due to a small potential hollow. By increasing temperature, the adsorption on the wall of ZSM-5 becomes favorable in equilibrium with the alkyl-OD adsorption.

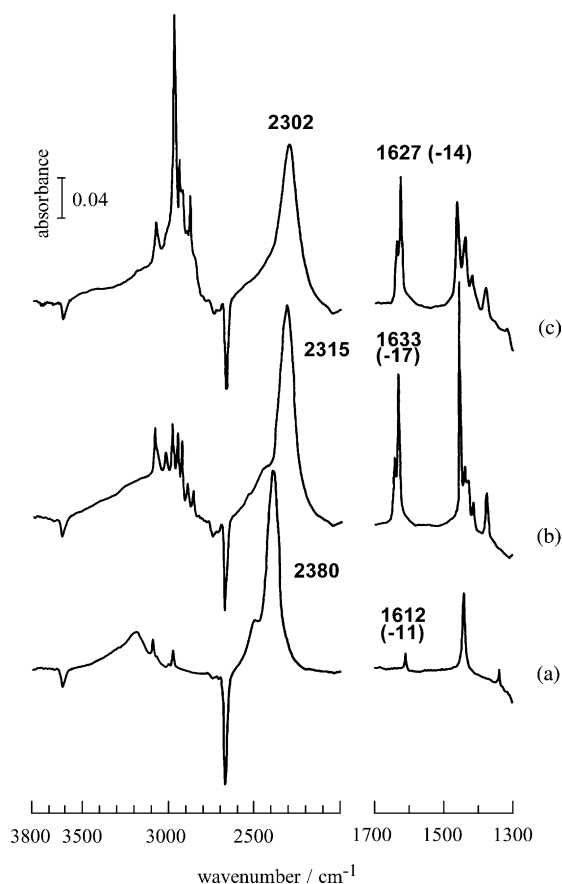


Fig. 4. IR spectra of ethene (a), propene (b), and 1-butene (c) adsorbed on D-ZSM-5 at around 200 K.

Above 173 K, gradual transformation of the adsorption on the wall to the π -complex is observed by increasing temperature in evacuation. It is noticed from the unchanged intensity of bands at 1400–1600 cm^{-1} that the amount of adsorbed 1-butene stayed constant from 173 to 206 K. By increasing temperature, hydrogen-bonded OD band in this π -complex gradually appeared. Simultaneously, the conversion of C=C band in peak position was observed from 1641 to 1627 cm^{-1} . The 1627 cm^{-1} band is assigned to the π -complex. Therefore, the adsorption on the wall of ZSM-5, which was in equilibrium with alkyl-OD adsorption, was found to be transformed to the more stable π -complex. In addition, thermal conversion to the π -complex indicates that the formation of π -complex was an activation process.

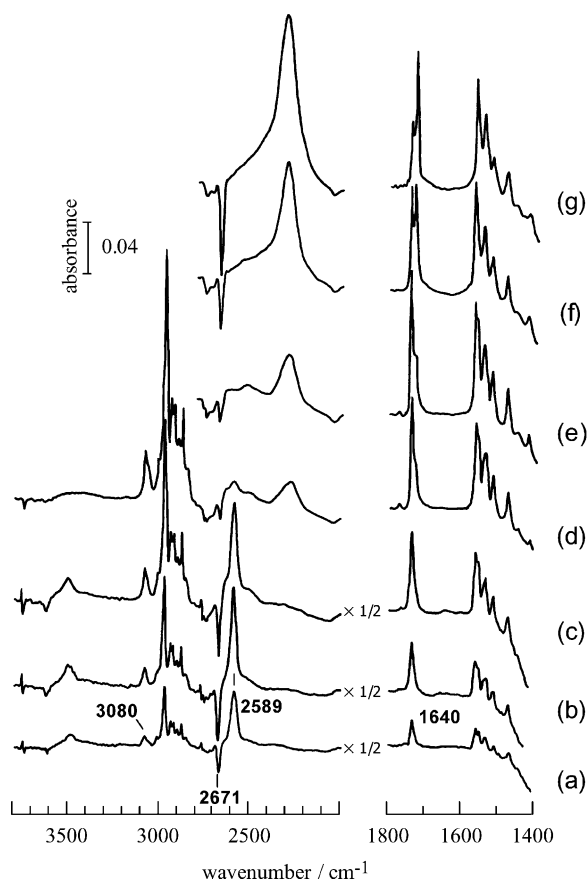


Fig. 5. IR spectra of 1-butene adsorbed on D-ZSM-5 at 155 K followed by evacuation and heating at 155 K (a), 160 K (b), 166 K (c), 173 K (d), 185 K (e), 203 K (f), and 206 K (g).

The overall transformation of the adsorption structure involving the π -complex is shown in Fig. 6. The adsorption on the wall, which is unrelated to the acidic OD groups, and the weakly interacted alkyl-OD adsorption are in equilibrium, and the alkyl-OD complex is preferentially observed at lower temperature region due to a small potential hollow. The adsorption on the wall becomes dominant at around 180 K, while the alkyl-interacting 1-butene overcomes an activation barrier to change the position of adsorption within a molecule to the most stable π -complex. As a result, 1:1 conversion of the wall adsorption to the π -complex is apparently observed. These adsorption structures of olefins on zeolites were experimentally found for the first time in this study, which would be beneficial information to molecular dynamics (MD)

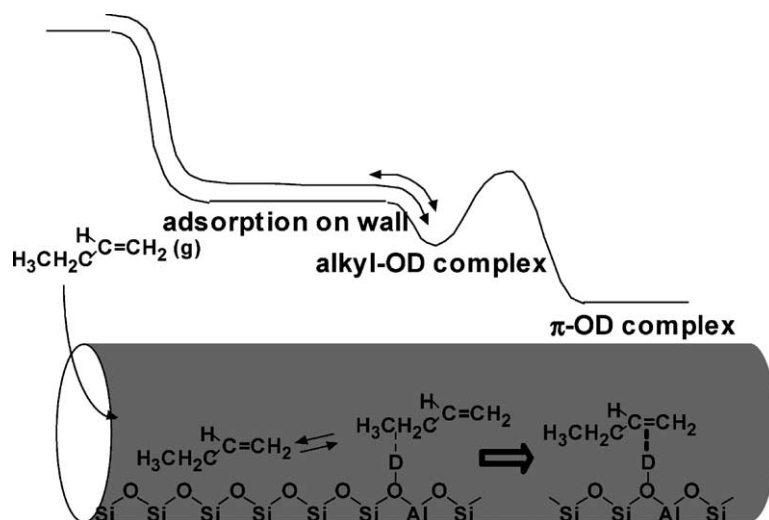


Fig. 6. Energy diagram and illustration of adsorption of 1-butene in a micropore of D-ZSM-5.

simulations on diffusion of hydrocarbons on zeolites. The height of the activation energy relies on the pore size of zeolites. The size of the pore, the size of the radius of curvature in other words, gives the activation barrier for the formation of the π -complex. This is easily imagined considering the fact that such an activation energy does not exist on flat surfaces. Therefore, the observed activation energy is attributable to the porous structure where the adsorption sites exist.

On MOR, which has larger pores than ZSM-5, only the π -bonded 1-butene was observed due to its larger radius of curvature (Fig. 7A). Therefore, the activation energy for the formation of π -complex on MOR is regarded as much smaller than that on ZSM-5. When it comes to FER with much smaller pores, rates of formation of π -complex was experimentally observed at a considerably high temperature, and large differences among the *n*-butene isomers were found (Fig. 7B). The rate determining step in this case is well interpreted as diffusion of olefin molecules to the acidic OH groups inside the small pores: *trans*-2-butene with smaller molecular diameter easily diffuse from on OH groups to another in the cage of FER, while more bulky 1-butene and *cis*-2-butene should overcome the energy barriers to diffuse in the small pore channels [15]. In this way, by low-temperature observation, various adsorption structures and the details of the behavior of olefin molecules were clarified.

3.3. Isomerization of 1-butene on D-ZSM-5

On zeolites, ethene and propene, which adsorb on the acidic OH or OD groups in equilibrium with other types of adsorption, only desorb by increasing temperature in evacuation, while polymerization takes place in the presence of gaseous molecules at room temperature. On the other hand, 1-butene isomerized to 2-butene below 230 K under evacuation, and dimerized at room temperature.

One of the acid-catalyzed isomerizations of olefins, the double bond migration (DBM) of 1-butene to 2-butene, is known to proceed by the mechanism established in solution chemistry is shown in Fig. 8A. First, a proton attacks the double bond of 1-butene and is involved in the carbenium intermediate. Then, the carbon three releases a proton, forming a new double bond in the second position. In this mechanism, if deuterium is used as a Brønsted acid, it is involved in the first methyl group and the isotope exchange of acid is accompanied. The protonated species, namely carbenium ion, is regarded as important intermediates for many acid-catalyzed reactions. In Fig. 8B a stepwise reaction mechanism of DBM of 1-butene on a deuterated Brønsted acid site of zeolite is shown, assuming the same mechanism as that in Fig. 8A. First, 1-butene hydrogen-bonds to the isolated OD group, and the deuterium is involved in the intermediate; whether

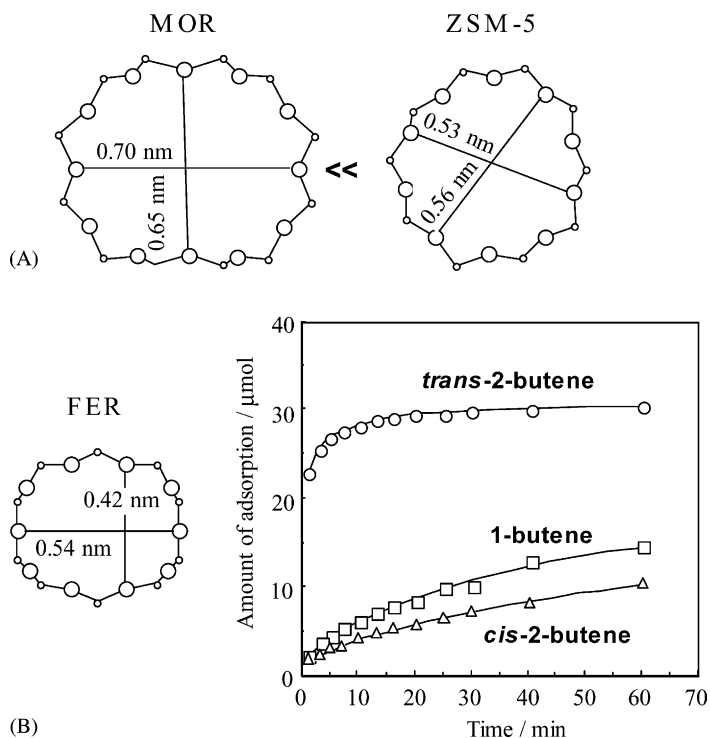


Fig. 7. Comparison of pore size and activation energy for the formation of π -OH (OD) adsorption complex between mordenite and ZSM-5 (A), and pore size and time course of butene adsorption on ferrierite at around 200 K (B).

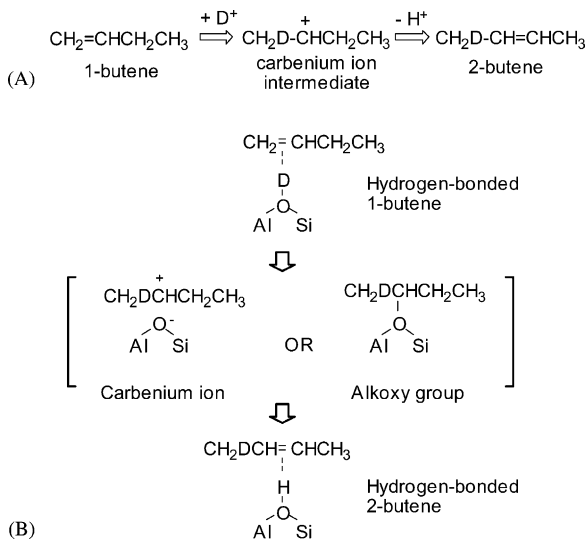


Fig. 8. Mechanism of double bond migration of 1-butene to 2-butene established in solution chemistry (A), and that on a deuterated Brønsted acid site of zeolite (B), assuming the same mechanism as that in (A).

carbenium ion or alkoxy group. Finally, proton is given back to the zeolite from the carbon three. As a result, deuterium is involved in the product, and the acidic OD group is isotope exchanged to OH. However, unexpected reaction was found as introduced later on.

A small amount of 1-butene was introduced to D-ZSM-5 below 150 K and was immediately evacuated. The amount of adsorption was limited to less than 80% of the acidic OD groups at each experiment. In that condition, the intermolecular interaction was minimized. IR spectra were observed during stepwise thermal reaction at a heating rate of 6 K min^{-1} .

IR spectrum of adsorbed 1-butene heated to 204 K is shown in Fig. 9a. As mentioned previously, the stable π -complex, adsorption of olefin with its C=C bond interacting with the acidic OD groups, is observed. The IR spectrum of the π -complex of adsorbed 1-butene is characterized by bands of olefinic CH stretching, C=C stretching at 1627 cm^{-1} and skeletal vibrations. The other C=C stretching band at 1641 cm^{-1} is due to weakly adsorbed species (mentioned earlier).

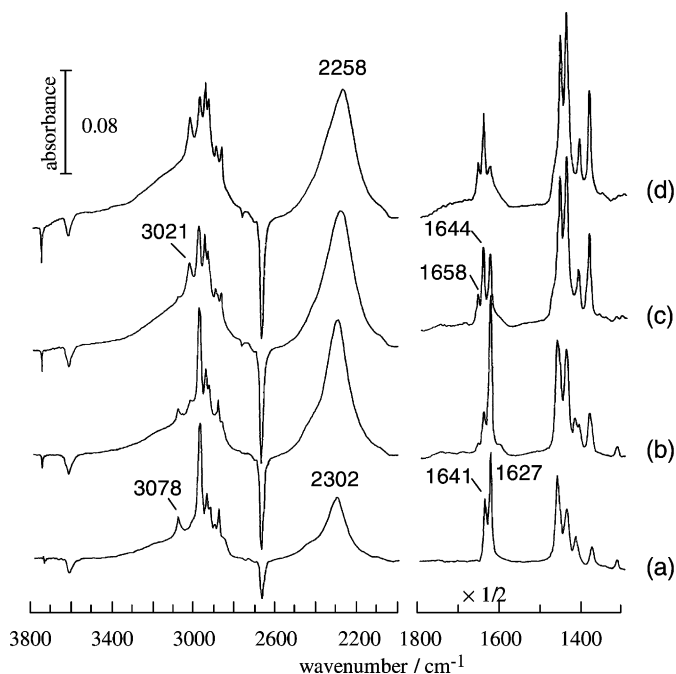


Fig. 9. IR spectra of 1-butene adsorbed on D-ZSM-5 at 204 K (a) and its thermal change at 212 K (b), 222 K (c), and 230 K (d).

By increasing temperature, change of IR spectra is observed. All the characteristic bands of the adsorbed 1-butene gradually decreased and almost disappeared at 230 K. Alternatively, new bands appeared and increased in intensity; an olefinic CH stretching band at 3021 cm^{-1} and two bands in C=C stretching region at 1658 and 1644 cm^{-1} . The skeletal vibrations appeared differently at higher temperatures. These results indicate the reaction of the most part of the adsorbed 1-butene below 230 K. It should be noted that the hydrogen-bonded OD band remained after the reaction, slightly shifting to lower frequency side, from 2302 to 2258 cm^{-1} in Fig. 9. The band due to hydrogen-bonded OH groups was not evidently observed at 230 K. In other words, the reaction of 1-butene proceeds without isotope exchange of Brønsted acid sites. When the spectrum of the reaction product (Fig. 9d) was compared with those of *cis*- and *trans*-2-butenes adsorbed on D-ZSM-5, the reaction product was found to be the mixture of *cis*- and *trans*-2-butenes; *cis*- and *trans*-2-butenes showed their C=C stretching bands at 1644 and 1658 cm^{-1} , respectively, and the hydrogen-bonded OD bands appeared at almost the same frequency at around 2260 cm^{-1} .

It should be mentioned that the isotope exchange reaction of the hydrogen-bonded OD groups took place above 230 K, while the DBM of 1-butene was observed below 230 K on D-ZSM-5 with no Lewis acid sites. Therefore, one comes to the conclusion that adsorbed 1-butene was converted to either *cis*- or *trans*-2-butene on D-ZSM-5 below 230 K in the absence of proton transfer from D-ZSM-5.

For clarification of the driving force of the DBM of 1-butene observed on D-ZSM-5, two factors of zeolites are varied; pore size and acid strength. The small pore size may result in the secondary interaction of the adsorbed molecule, or the strong acidity of the OH groups themselves may induce such an unusual reaction. MOR shows equally strong or stronger Brønsted acidity, and possesses larger pore size than those of ZSM-5. Therefore, the secondary interaction, if exists, would be avoided. The temperature-dependent IR spectra of the adsorbed 1-butene were exactly the same as those of D-ZSM-5: DBM of 1-butene to *cis*- and *trans*-2-butenes was observed in the absence of H/D exchange reaction at lower temperature range than the isotope exchange. This clearly indicates that the DBM on DM20 also occurred without proton transfer from

OD groups to 1-butene. Thus, the secondary interaction of the adsorbed molecule with the lattice atoms is excluded from the cause of the reaction.

The acidity of OH groups of Y zeolites is known to be weaker than ZSM-5 and MOR. The adsorption and reaction of 1-butene on a FAU zeolite, HY5.6, was studied to clarify the importance of strong acidity. Although the DBM was gradually observed, the decrease of the hydrogen-bonded OD groups was observed in the same temperature range. The same results were obtained by using another FAU zeolite with a different Si/Al ratio. Therefore, the proton-transferred intermediate such as alkoxy or carbenium species could not be excluded from the candidates of the intermediate of the DBM on weakly acidic Brønsted acid sites of zeolites.

In summary, the DBM of 1-butene to 2-butene was found by IR method to proceed in the absence of the proton transfer from the acidic OD groups of zeolites at low temperature. The reaction was clearly distinguished on strongly acidic BAS of zeolites (ZSM-5 and MOR) from the H/D isotope exchange reaction of the OD groups. This is not expected to occur if the alkoxy or carbenium intermediate was assumed. The observed reaction path was not interpreted by the conventional acid-catalyzed mechanism. This could be attributed to a unique property of solid surfaces, or may imply the presence of another type of active sites than the acidic OD groups. Details may be clarified by additional experiments as well as by quantum chemical calculations.

3.4. Dimerization of *n*-butene on D-ZSM-5 at room temperature

At higher temperatures, the intensity of the hydrogen-bonded OD band decreased accompanied by the growth of the hydrogen-bonded OH band (not shown). This indicates the occurrence of the isotope exchange reaction of the acidic OD groups and adsorbed species. In the temperature range of isotope exchange reaction, almost all the adsorbed 1-butene already transformed to the adsorbed 2-butenes. Therefore, the isotope exchange reaction of the hydrogen-bonded OD to OH groups is resulted from the reaction with 2-butene. As the isotope exchange reaction proceeded, the amount of 2-butene decreased, as confirmed as dimerization by our studies conducted at higher temperatures as

shown later. Therefore, it is considered that once the proton transfer occurs, facile intermolecular reaction takes place as generally conceived as mediated by either the alkoxy or the carbenium species.

Since the H/D isotope exchange results in the complexity of spectral appearance, the reaction of 2-butene at room temperature was quantitatively studied by using H-form ZSM-5. The H-ZSM-5 sample was exposed to 0.1 Torr (1 Torr = 133.322 Pa) of 1-butene and the system was immediately evacuated. About 80% of the isolated OH groups of Brønsted acid site was occupied by the adsorbates. The IR

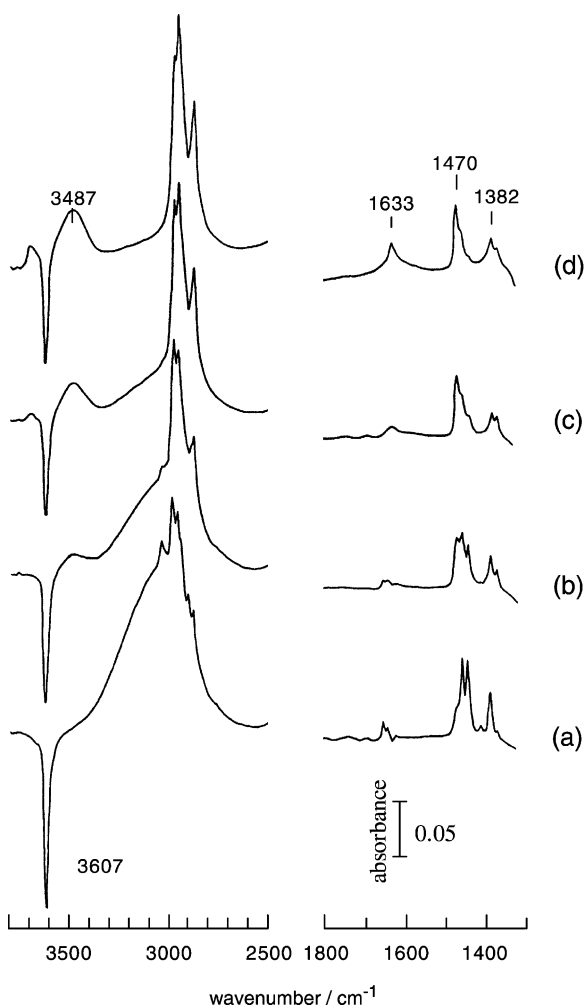


Fig. 10. IR spectra of 1-butene adsorbed on H-ZSM-5 at room temperature: soon after the reaction (a), 10 min (b), 30 min (c), and 120 min (d) after the reaction started.

spectrum of the adsorbed species formed by 1-butene adsorption at room temperature is shown in Fig. 10a, which are assigned to the 2-butenes. The IR band of the hydrogen-bonded OH groups appeared at ca. 3100 cm^{-1} . Then, the system was maintained in evacuation for 120 min at the same temperature (Fig. 10d). The hydrogen-bonded OH groups observed at ca. 3100 cm^{-1} disappeared after 120 min, and a small band at ca. 3500 cm^{-1} appeared. Simultaneously, the intensity of the negative band due to the isolated OH groups at 3607 cm^{-1} decreased. The bands of the adsorbed species also gradually changed in the CH stretching ($2800\text{--}3100\text{ cm}^{-1}$), C=C stretching ($1600\text{--}1700\text{ cm}^{-1}$) and deformation ($1200\text{--}1500\text{ cm}^{-1}$) regions. When 1-butene was introduced again onto the H-ZSM-5 after 120 min reaction (Fig. 10d), the same change in the spectra was observed by taking the Fig. 10d as a background spectrum. This implies that the same reaction proceeded on vacant sites. In other words, the formed species observed in Fig. 10d are not living intermediates but considerably stable species.

The change of the integrated intensity of the isolated OH band of Brønsted acid sites in the time course of the reaction observed in Fig. 10 and successive reaction is plotted in Fig. 11. The amount of the isolated OH groups recovered as the reaction proceeded after

it had sharply decreased by butene adsorption. The extent of the recovery was estimated by an extrapolated value of the time 0 as about 40–50% of the initial decrease. It is noted that further recovery was not observed after the reaction completed. Therefore, the reaction of butenes on H-ZSM-5 at room temperature is deduced as dimerization assuming the homogeneous reactivity of adsorbed butenes. In the case where oligomerization or polymerization proceeds, more amount of the isolated OH groups than that in Fig. 11 may be recovered from hydrogen-bonded ones as a result of the decrease in the amount of the adsorbed butene.

For the second dosage of 1-butene the time course of the recovery of the isolated OH groups was also the same as the first as plotted in Fig. 11; about half of the isolated OH groups which was decreased by butene adsorption recovered from the hydrogen-bonded OH groups. This let us conclude that the reaction of the adsorbed butenes terminates at dimerization and that oligomerization or polymerization does not proceed at room temperature. As schematically described in Fig. 12, dimerization of π -bonded 2-butene releases a half of the strongly hydrogen-bonded OH groups into the isolated state.

The geometrical and adsorption structures of the produced dimer compound are then considered. The

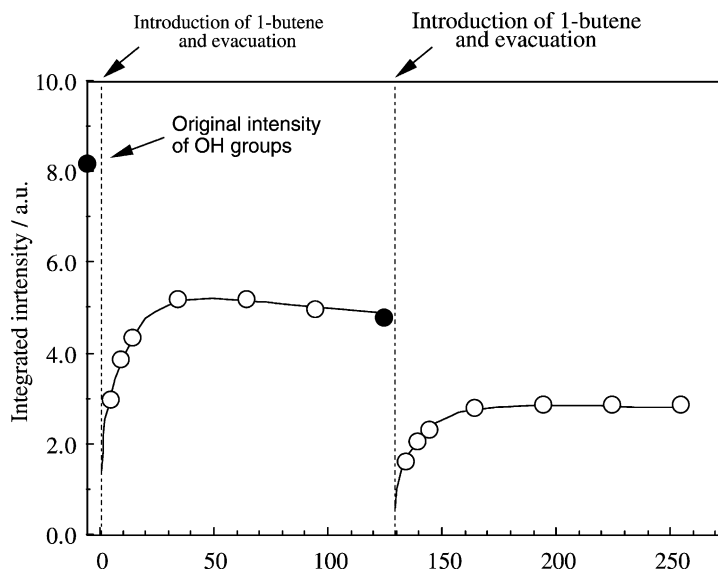


Fig. 11. Time course of the integrated intensity of the isolated OH groups of BAS on H-ZSM-5.

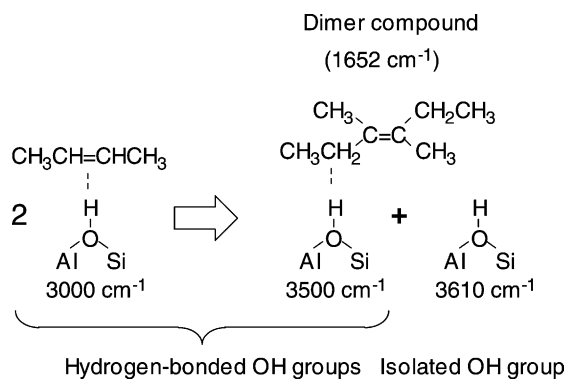


Fig. 12. Schematic illustration of dimerization of 2-butene on H-ZSM-5 at room temperature under evacuation.

characteristics of the IR spectrum (Fig. 10d) of the adsorbed dimer are as follows: (1) the hydrogen-bonded OH groups with the dimer was observed at around 3500 cm⁻¹, (2) a weak C=C stretching band was observed at 1633 cm⁻¹, and (3) any olefinic CH stretching band was not observed. The shift of ca. -100 cm⁻¹ of the OH band to low frequency region by hydrogen-bonding is identical to the adsorption of saturated hydrocarbons on H-ZSM-5, which indicated a weak hydrogen-bonding of OH groups of Brønsted acid site with an alkyl group [16,17]. The IR band of the hydrogen-bonded OH groups with the dimer compound was observed in the same manner, and adsorption of the dimer is regarded as a weak hydrogen-bonding between OH groups and alkyl chains of the dimer. The product of the dimerization of 2-butene is regarded as being branched, and the weak C=C stretching band of it indicates its highly symmetric structure. If one notices that the hydrogen-bonding of OH groups is not what is observed with the C=C bond but that with the alkyl chains of the dimer, the C=C bond is considered to be sterically hindered to approach the OH groups. Combining the fact that the dimer did not show any olefinic CH stretching band above 3000 cm⁻¹ with the previously mentioned consideration, the structure of the dimer is expected to be that as shown in Fig. 12.

Because the C=C bond of the produced dimer was found to be hindered to hydrogen-bond with the OH groups of Brønsted acid site due to the steric hindrance, protonation of the dimer would not occur at room temperature, and further reactions such

as oligomerization and polymerization would not proceed.

3.5. Further studies

3.5.1. Reaction of isobutene and cyclic olefins

On the purpose of observation of carbenium cations or alkoxy intermediates, isobutene was also studied, which was expected to form stable monomolecular intermediates. However, adsorbed species observed at the very beginning of the reaction in evacuation below 200 K were already dimerized species, which were confirmed by adsorption of branched C₈ olefins (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene), expected dimer products of isobutene. The expected monomeric isobutoxy groups were not observed, most probably due to the rapid migration of olefin molecules and the high reactivity of the protonated species.

Noting that the detected saturated and unsaturated carbenium cations by NMR, which were formed through further reactions after initial proton transfer at considerably high temperatures, have cyclic structures [18,19], we expected to observe some of the cations by simple protonation of cyclic olefins on the acidic OH groups. 1-Methylcyclopentene and methylenecyclopentane were adsorbed on Y zeolites and formed the same initial reaction product, which was identified by an IR band at ca. 1510 cm⁻¹. Although the identical band at 1510 cm⁻¹ has been often observed and assigned to carbenium cations, the formed product in our study was assigned to the dimerized unsaturated cation by quantification of the acidic OH band as well as by UV-Vis spectroscopy [20,21]. Even at temperatures below 200 K, several reactions were found to proceed on zeolite, resulting in the complexity of zeolite chemistry.

3.5.2. Observation of practical catalysis of zeolites at high temperature in flow system

By low-temperature observation, motions and reactions of hydrocarbons on zeolites, which require small activation energies are observed. Although these are fundamental processes, overall reactions at high temperature include further elemental steps with larger activation energies. Therefore, understanding of the behavior of the adsorbed species at high temperatures is indispensable in order to realize the real catalysis of

zeolites. On this basis, isomerization of *n*-heptane on Pt/H β zeolite is now under investigation. A cell with very short (2 mm) optical path was equipped in the flow system, which was connected to a gas chromatograph for this study. This system allows us to observe the surface species during the reaction in the absence of hindrance by IR absorption of gaseous molecules and to detect the reaction product simultaneously. For skeletal isomerization of *n*-alkane, coke formation proceeds seriously in the absence of Pt loading as well as hydrogen co-flow, resulting in catalyst deactivation. The formation of coke could be only found by post-reaction analysis of the used catalysts, and when and how the coke deposits are not well known. As a primitive results, stepwise coke formation through olefinic species and polyolefins was observed during the reaction on rapidly deactivated catalysts, while only the olefinic species was found on the catalyst with long life time. Details on the mechanism are now under investigation using isotopes.

4. Conclusion

Details of the adsorption and reactions of olefins on zeolites were clarified by using low-temperature IR spectroscopy. The series of studies were started on the purpose of understanding the reactivity of the acidic OH groups on zeolites, representatives of solid Brønsted acids. We were motivated to detect the initial mono-molecular reaction product of olefin protonation on the acidic OH groups of zeolites. However, it was not successful in the present study. The short-lived mono-molecular intermediates are expected to be discovered by time-resolved IR laser spectroscopy. In situ IR observation is now extended to the practical catalysis proceeding at high-temperature range, which should bring new information different from that so far known.

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