DoubleBond Migration of an Olefin without Protonated Species on H(D) Form Zeolites

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A novel reaction path was found for the double-bond migration (DBM) of 1-butene on very strong Brønsted acid sites (BAS) of zeolites, ZSM-5 and mordenite (MOR), in the absence of protonation below 230 K with the activation energies of 49 ± 4 kJ·mol^{-1} on D-ZSM-5 and 38 ± 8 kJ·mol^{-1} on D-MOR (DM20). By using deuterated zeolites, it was proved that the protonated intermediate is not essential to the conversion of the 1-butene to the hydrogen-bonded *cis-* and *trans*-2-butenes on the BAS of ZSM-5 and MOR. If the widely accepted protonated intermediate is assumed, the acidic OD groups should be converted to OH groups upon the DBM of 1-butene to 2-butenes. Nevertheless, the OD groups of zeolites forming 1:1 complex with 1-butene remained unchanged even after the double-bond migration. The isotope exchange reaction of OD groups due to the proton transfer occurred at higher temperature than the DBM. However, the DBM on a deuterated faujasite (FAU) zeolite (DY5.6 and DY4.8) proceeded accompanied by the H/D exchange reaction of the acidic OD groups, suggesting that the protonated intermediate is essential for the reaction on rather weak BAS. Thus, the existence of a new type of reaction catalyzed by very strong BAS is demonstrated, which takes place more facilely than the proton transfer.

1. Introduction

Solid-catalyzed reactions are utilized in syntheses of many compounds and are now indispensable for industrial chemistry. Zeolites, which are a family of aluminosilicates with characteristic porous structures, are one of the most attractive materials as catalysts. The acidity of zeolites is regarded as the origin of various acid-catalyzed reactions on zeolites and classified into Brønsted and Lewis acid sites (BAS and LAS), respectively. BAS exist as bridging OH groups between Al and Si atoms, and LAS are known to be generated by dehydration of BAS from zeolites at higher temperature.[1]
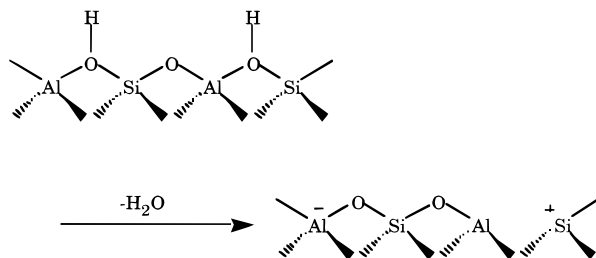
The reactivity of the acidic OH groups and the reaction mechanisms on the zeolites have been studied by indirect methods for a long time, and reaction mechanisms similar to those established in homogeneous chemistry have been assumed without any direct evidence.[2,3] Recently, direct observation of both BAS themselves and their interaction with adsorbed molecules have become possible by IR and NMR methods.[4−6] On the other hand, the assessment of the proposed models and activated complexes (the intermediates) of the reactions greatly relies on the quantum chemical calculations that also have been recently developing.[7−9]

The double-bond migration (DBM) of olefins are widely known to be catalyzed by Brønsted acids. Its reaction mech-

anism has been postulated to proceed via protonated intermediates as follows:

$$CHR{=}CHCH_2R' + H^+ \rightleftarrows CH_2R{-}\overset{+}{C}HCH_2R' \rightleftarrows$$
$$CH_2R{-}CH{=}CHR' + H^+$$
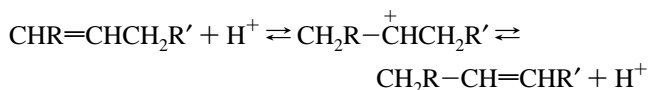
The protonated species, namely carbenium ions, are regarded as important intermediates for many acid-catalyzed reactions.[2,3] The importance of the protonated intermediates and similar mechanism are also emphasized for catalysis of other solid acids.[4,9,10]

We have studied the interactions of OH (OD) groups of BAS on zeolites with small molecules by means of IR spectroscopy and have attempted to understand the essential features of the interactions[11−14] as well as their reactivity.[15−17] Our work on the adsorption and reaction of some molecules on zeolites has recently been extended to those of olefins. Here, we report unusual results of one of the reactions of olefins, DBM, observed by IR spectroscopy. The results suggest the existence of a novel route for the DBM on BAS of zeolites, which cannot be interpreted by the widely accepted proton-transfer mechanism.

2. Experimental Section

The H-ZSM-5 zeolite (Si/Al = 50) and Na-ZSM-5 (Si/Al = 76.6) were supplied by Sumitomo Chemical Co. Ltd., and a mordenite (HM-20, Si/Al = 10) and Y-type zeolites (HY 5.6, Si/Al = 2.8; HY4.8, Si/Al = 2.4) were offered by the Catalysis Society of Japan. 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. The sample disks of H(D)-ZSM-5[11] and H(D)M-20[12] were treated under the condition that no LAS were produced. Deuteration of H-ZSM-5, HM-20, HY5.6, and HY4.8 to their D-forms was conducted by exposing the sample disk to D$_2$ at 673 K for 1 h. About 90% of Brønsted acidic OH groups were converted to OD groups by this treatment. A small amount of butenes (less than 0.3 Torr for H(D)-ZSM-5 and less

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TABLE 1: Assignment of IR bands of 1- and 2-Butenes on ZSM-5

|	1-butene[d]			cis-2-butene[e]		trans-2-butene[f]	
assignment	Ar matrix[a,b]	on ZSM-5	assignment	Ar matrix[a]	on ZSM-5	Ar matrix[a]	on ZSM-5
=CH$_2$ a-str.	3090	3078	CH str.	3025, 3052	3024	3044, 3036	3022
CH str.	3018		CH$_3$ a-str.	2930, 2948	2924, 2943	2948, 2976	2938, 2966
=CH$_2$ s-str.	2993			2992, 2988	2986		
CH$_3$ a-str.	2980	2972	{2 × CH$_3$ a-def.}	2902, 2871	2866	2892, 2865	2887, 2860
CH$_2$ a-str.	2936	2940, 2924,	{CH$_3$ s-str. }	2894, 2864			
CH$_3$ s-str.	2904	2899, 2879					
CH$_2$ s-str.	2886, 2889						
C=C str.	1641	1627	C=C str.	1668	1645	(1682)[c]	1657
CH$_3$ a-def.	1468	1464	CH$_3$ a-def.	1444, 1454, 1458	1444, 1457	1455	1440
CH$_3$ a-def.	1459						
CH$_2$ bend.	1439, 1444	1441	CH$_3$ s-def.	1384, 1408	1386, 1407	1379	1382
=CH$_2$ in-plane bend.	1414, 1421	1419					
CH$_3$ s-def.	1378	1379					
CH$_2$ wag.	1316, 1323	1316					

[a] Reference 18. [b] The former numbers are for the *gauche*-form and the latter for the *trans*-form. [c] IR inactive mode, and the presented number was observed by Raman spectroscopy. [d] The spectrum measured at 204 K was used for the frequencies. [e] The spectrum measured at 217 K was used for the frequencies. [f] The spectrum measured at 215 K was used for the frequencies.

than 1.2 Torr for the others) was introduced below 150 K and was immediately evacuated. About 20−80% of BAS are occupied by the adsorbate, and in that condition the intermolecular interaction was avoided. The IR cell was then gradually heated (ca. 6 K·min^{-1}) while evacuating. If the reactant remains in gas phase or the adsorption is conducted at higher temperatures, protonation of the adsorbed species and reaction of the protonated species with the adsorbed or gaseous molecules occur simultaneously, and thus, interpretation suffers from the complexity of the observation. On the other hand, this method enables us to extract the initial interaction of BAS and adsorbed olefins followed by stepwise thermal reactions.

3. Results and Discussion

Adsorption of 1-Butene on D-ZSM-5. 1-Butene adsorbed on D-ZSM-5 at 204 K gives an IR spectrum as shown in Figure 1a. Since the spectrum of D-ZSM-5 measured in the absence of adsorbates was subtracted, the decreased band of free OD groups (2671 cm^{-1}) is shown as a reverse peak. Alternatively, a broad band due to the hydrogen-bonded OD groups with adsorbed 1-butene appeared at 2302 cm^{-1}. The IR spectrum of adsorbed 1-butene is characterized by bands of olefinic CH stretching at 3078 cm^{-1}, C=C stretching at 1627 cm^{-1}, and skeletal vibrations between 1500 and 1300 cm^{-1}. The other C=C stretching band appeared at 1642 cm^{-1}, which is the same frequency as that observed for 1-butene in Ar matrix.[18] This band is due to weakly adsorbed species, probably on frameworks of ZSM-5, and was dominant below 200 K. However, the weakly adsorbed species decreased as the temperature was increased and converted to form the 1:1 π-complex with BAS as shown below. The hydrogen-bonded 1-butene in 1:1 π-complex with BAS shows its C=C stretching band at lower frequency (1627 cm^{-1}) than the weak adsorbates as a result of interaction of the π-electron of 1-butene with BAS. The assignments of the observed bands of the adsorbed 1-butene on BAS are listed in Table 1.

At 212 K, the IR spectrum started to change from that measured at 204 K as noticed in the olefinic CH stretching above 3000 cm^{-1} and the skeletal vibration range; a new band appeared at 3021 cm^{-1}, the intensity ratio of two bands at higher frequency, namely at 1464 and 1441 cm^{-1}, in skeletal vibration range changed, and an additional band at 1411 cm^{-1} appeared. The increase of the peak intensity of the reverse band of the isolated OD band (BAS) as well as those of the bands at 2302 and 1627 cm^{-1} at 212 K is attributed to the increase of the
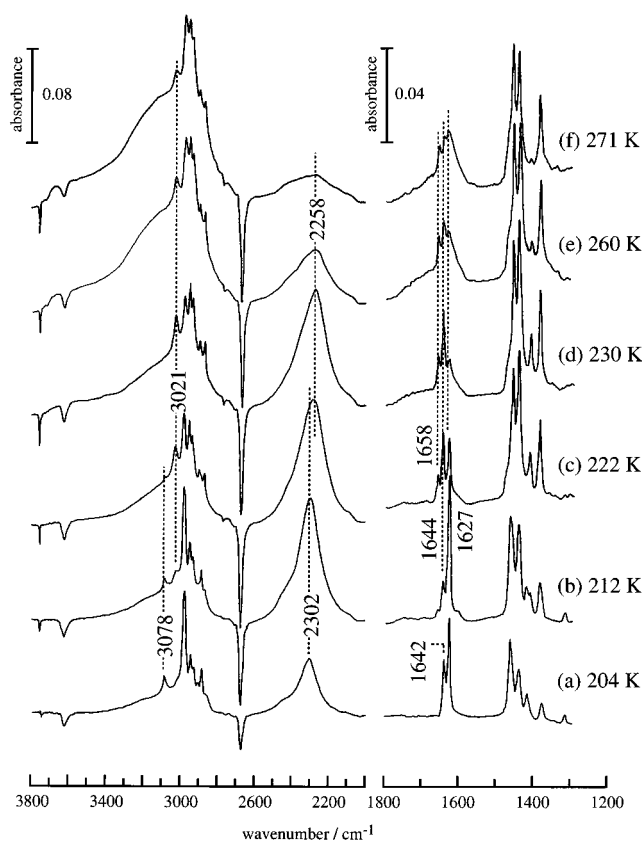
Figure 1. IR spectra of 1-butene adsorbed on D-ZSM-5 at 204 K (a) and its thermal change at 212 K (b), 222 K (c), 230 K (d), 260 K (e), and 271 K (f).

amount of the 1:1 π-complex of 1-butene with BAS. On the other hand, the band at 1642 cm^{-1} due to the weakly adsorbed species decreased. This is because the weakly adsorbed species became mobile by the temperature increase and transferred into the 1:1 π-complex. (Note that intensities of the other bands due to 1-butene did not change greatly.) Further increase in temperature to 230 K caused complete change in IR spectra, where all the characteristic bands of the adsorbed 1-butene (Figure 1a) almost disappeared. On the other hand, new bands appeared and increased in intensity: an olefinic CH stretching band at 3021 cm^{-1}, two bands in C=C stretching region at 1658 and 1644 cm^{-1}, and those in skeletal vibration region. The great decrease of the bands of 1-butene indicates the disappearance of the most part of 1-butene in 1:1 π-complex with BAS, and
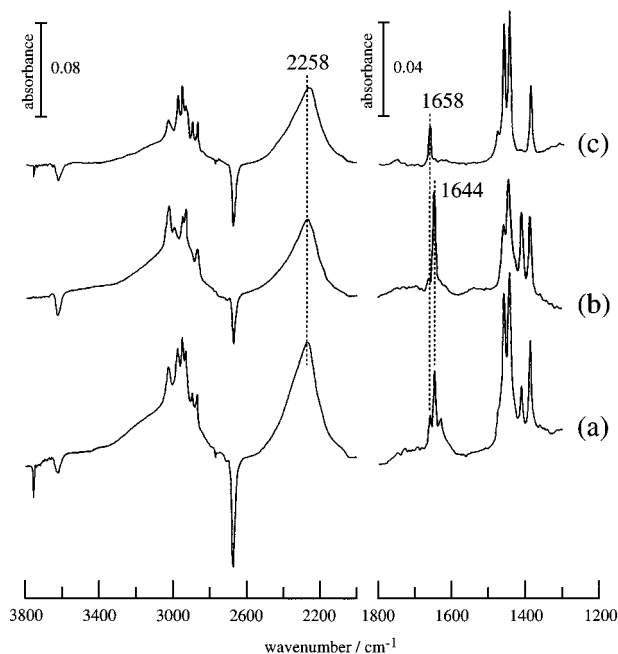
Figure 2. Comparison of IR spectra of the reaction product and those of the 2-butenes adsorbed on D-ZSM-5: the reaction product (a), *cis*-2-butene at 217 K (b), and *trans*-2-butene at 215 K (c).

Figure 3. Temperature dependence of relative amount of the adsorbed species during thermal reaction of 1-butene on BAS of D-ZSM-5.

the appearance of the alternative bands and their increase means the generation of new adsorbed species from 1-butene as a result of a reaction below 230 K. It should be noted that the hydrogen-bonded OD band remained after the reaction although it shifted from 2302 to 2258 cm^{-1}. In the OH stretching region at the same time, the band due to hydrogen-bonded OH groups (expected to appear at around 3100 cm^{-1}) was not observed. In other words, the reaction of 1-butene proceeds without H/D isotope exchange of OD groups of BAS. At higher temperatures than 230 K, the intensity of the hydrogen-bonded OD band decreased accompanied by the growth of the hydrogen-bonded OH band around 3100 cm^{-1}, indicating the occurrence of the H/D isotope exchange reaction.

The spectrum of the reaction product (Figure 1d) is compared with the reference spectra of *cis*- and *trans*-2-butenes adsorbed on D-ZSM-5 around 220 K in Figure 2. The spectrum in Figure 2a represents the reaction product from 1-butene at 230 K, and those of parts b and c in Figure 2 were due to *cis*- and *trans*-2-butenes adsorbed on D-ZSM-5 under evacuation. *Cis*- and *trans*-2-butenes show their C=C stretching bands at 1644 and 1658 cm^{-1}, respectively, and the hydrogen-bonded OD bands appeared at almost the same frequency. The assignments of the vibrational bands due to the 2-butenes are summarized in Table 1. The C=C stretching of 1- and *cis*-2-butenes appear at 1641 and 1668 cm^{-1} in Ar matrix, while that of *trans*-2-butene is IR inactive (1682 cm^{-1} by Raman). For the adsorbed butenes they were observed at 1627, 1645, and 1657 cm^{-1}, shifting to lower frequencies and becoming IR active. The shifts of their C=C stretching bands are the evidence of the existence of direct interactions of C=C bonds with OD groups of BAS. Therefore, it is possible to analyze all the observed butenes quantitatively by using the integrated absorbance of the C=C stretching bands. By comparison of the IR spectrum of the reaction product with those of 2-butenes (Figure 2), it becomes clear that the adsorbed species produced from 1-butene are the mixture of *cis*- and *trans*-2-butenes. The shift of the hydrogen-bonded OD stretching from 2302 cm^{-1} (204 K) to 2258 cm^{-1} (230 K), which was observed when the reaction of the adsorbed
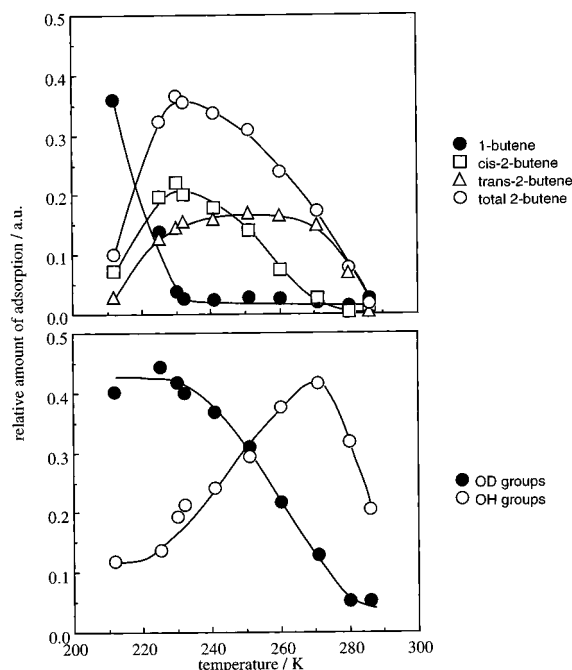
1-butene occurred, further confirms the production of 2-butene. Great attention must be paid to the fact that the hydrogen-bonded OD groups did not convert to OH ones below 230 K even after the conversion of the adsorbed 1-butene to 2-butenes. It is noted that the reaction proceeds on D-ZSM-5 where no LAS exist. Therefore, it is concluded that adsorbed 1-butene was converted to either *cis*- or *trans*-2-butene on Brønsted acidic OD groups below 230 K in the absence of proton transfer from D-ZSM-5.
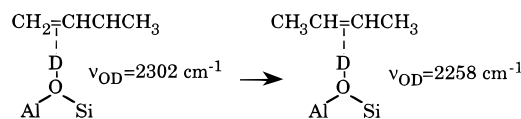

The temperature dependence of the integrated intensity of the characteristic bands of each species is shown in Figure 3. The intensity of the hydrogen-bonded OH band was integrated between 3550 and 3100 cm^{-1} with a horizontal base line not involving the olefinic CH stretching band, while the hydrogen-bonded OD band was integrated between 2600 and 2100 cm^{-1}. The C=C stretching bands of butenes, 1627 cm^{-1} for 1-, and 1644 cm^{-1} for *cis*-2-, and 1658 cm^{-1} for *trans*-2-butene, were used to estimate the amount of adsorption of butenes. The relative absorption coefficients of the three C=C stretching bands were obtained by normalization of the coverages of each species by the isolated OD band decreased upon adsorption of each species. Almost complete decrease of 1-butene and concurrent production of 2-butenes are clearly shown below 230 K where the amount of OD groups stays constant. On the other hand, above 230 K, the isotope exchange reaction of the hydrogen-bonded OD groups took place evidenced by the decrease of the OD groups and the simultaneous increase of the OH. In that temperature range 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 regarded as a result of the reaction with the adsorbed 2-butenes.

The isotope exchange reaction of BAS is generally conceived as mediated by either the alkoxyl or the carbenium species.[4,6,9,10]
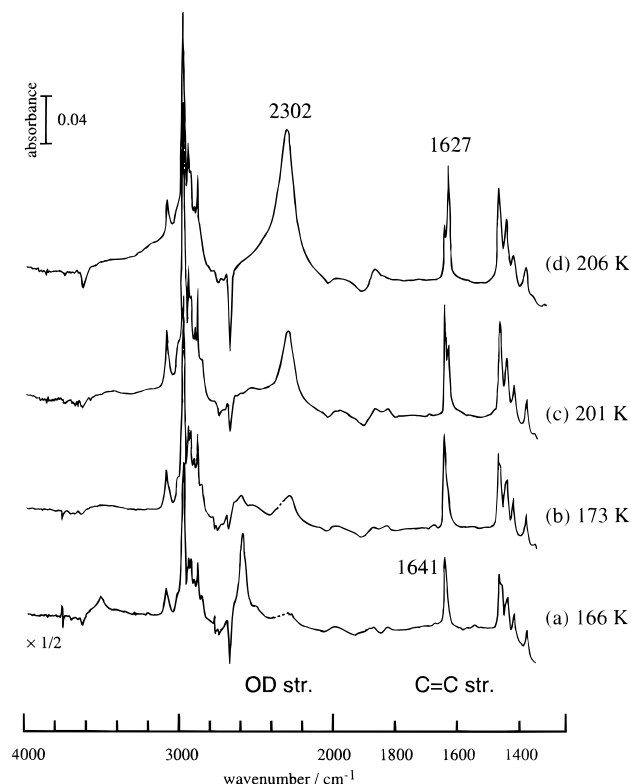
Figure 4. IR spectra of 1-butene adsorbed on D-ZSM-5 at 166 K (a), 173 K (b), 201 K (c), and 206 K (d).
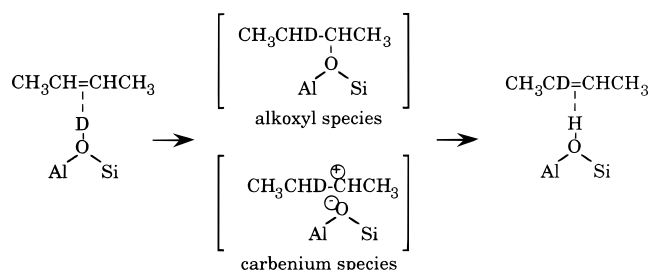

As the isotope exchange reaction proceeded, the total integrated intensity of the bands due to 2-butenes decreased (Figure 3). It is also noted in Figure 1 that the spectral feature especially in CH stretching region changed above 230 K. These results indicate that the reaction of 2-butene starts above 230 K accompanied by the isotope exchange reaction of BAS. It is again shown in Figure 3 that the DBM of 1-butene and the isotope exchange reaction of BAS are clearly distinguished by the reaction temperature. The latter reaction of 2-butene has been confirmed to be the dimerization of adsorbed 2-butene molecules by our studies conducted at higher temperatures (~300 K).[19]

A series of IR spectra of 1-butene adsorbed on D-ZSM-5 at much lower temperatures are shown in Figure 4. 1-Butene was introduced at ca. 140 K followed by evacuation and gradual heating to 206 K where DBM did not occur. At 166 K a small reverse band of BAS was observed that shifted to the hydrogen-bonded one at around 2600 cm^{-1}. The shift of the OD band is much smaller than that observed for the 1:1 π-complex with N$_2$,[11] indicating that the hydrogen bonding is very weak and totally different from the one observed at 2302 cm^{-1}. The C=C stretching band of 1-butene at 166 K appeared at the same frequency as that in Ar matrix. Therefore, the hydrogen-bonded 1-butene observed at 166 K is not forming a 1:1 π-complex with BAS but would rather bond with the methyl groups. Increasing the temperature to 173 K, the weakly hydrogen-
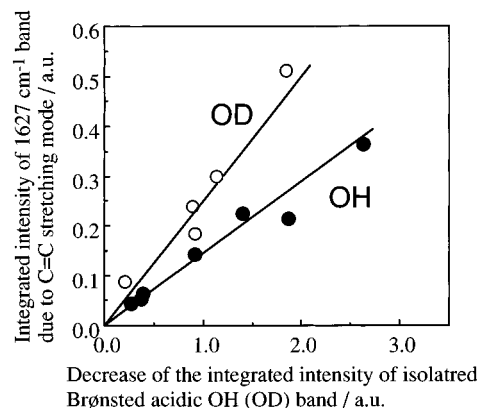

Figure 5. Correlation between the increase of the C=C stretching band at 1627 cm^{-1} and the decrease of the isolated OD band.

bonded OD groups disappeared and only a small amount of 1:1 π-complex was observed, while bands of the adsorbed 1-butene were evident. (The amount of adsorption increased due to desorption of the initially trapped 1-butene on the cell followed by readsorption onto D-ZSM-5 even in evacuation.) The 1-butene is, therefore, considered to be trapped at the framework of the zeolite. This type of adsorption, as well as the hydrogen bonding observed at 166 K, is regarded as much weaker than the 1:1 π-adsorption since all the bands stayed in the same frequencies as those in Ar matrix. By gradual heating above 180 K, conversion of the peak position of C=C stretching band was observed from 1641 to 1627 cm^{-1}, while the same intensity of the other bands was maintained. A slight shift of CH$_3$ deformation band at 1468 to 1464 cm^{-1} at 201 K was also observed. The conversion of C=C stretching band was accompanied by the increase of the reverse band of isolated OD groups of D-ZSM-5 and that of the hydrogen-bonded one. The 1:1 correspondence of the C=C stretching band at 1627 cm^{-1} and the reverse band due to the isolated OD (OH) groups is demonstrated in Figure 5, where each point was measured from a spectrum observed between 200 and 220 K. The linear correspondence of the C=C stretching band at 1627 cm^{-1} and the decrease of the isolated OD (OH) bands clearly indicate the 1:1 interaction of the adsorbed 1-butene showing its C=C stretching band at 1627 cm^{-1} with the OD (OH) groups of BAS.
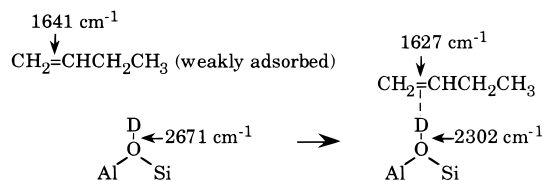
Moreover, only ca. 80% of the isolated OD groups were altered to the hydrogen-bonded ones in Figure 4d. Therefore, the DBM observed on OD groups is concluded not to proceed by intermolecular reaction but in each 1:1 complex of the adsorbed 1-butene and the OD group.

From the pore structure and the Si/Al ratio (50) of the presently used ZSM-5, each BAS is regarded as being well separated by the structure of ZSM-5. This distribution provides important information for both DBM of 1-butene and the dimerization. All the adsorbed 1-butene molecules were forming 1:1 complex with BAS separated from each other as mentioned above, and therefore, the intramolecular DBM of 1-butene on a BAS is supported. In other words, a possibility of the cause of the DBM by intermolecular reaction is further excluded. The beginning of dimerization upon proton transfer above 230 K evidences the occurrence of migration of the
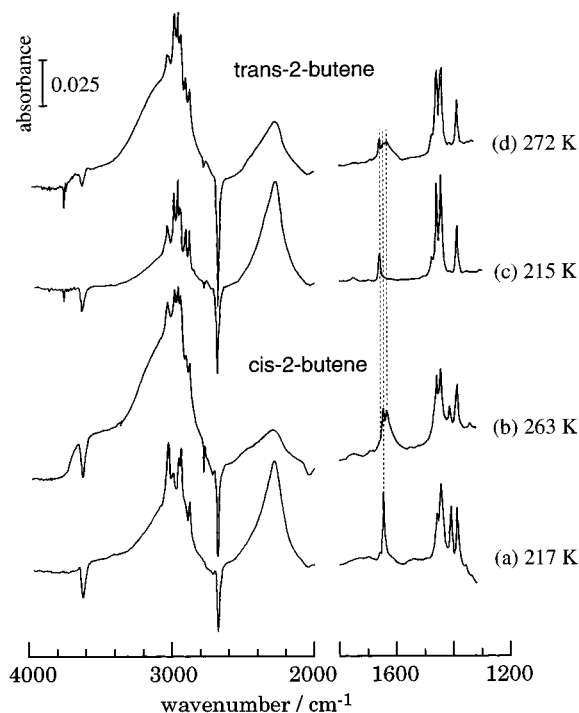
Figure 6. Change of IR spectra of the 2-butenes adsorbed on D-ZSM-5: *cis*-2-butene at 217 K (a) and 263 K (b) and *trans*-2-butene at 215 K (c) and 272 K (d).

adsorbed species. This was confirmed by the increase of the IR band of the isolated OH groups by the isotope exchange when the amount of adsorption of butenes was much smaller (not shown).

Adsorption and Reaction of *cis*- and *trans*-2-Butenes on D-ZSM-5. Both *cis*- and *trans*-2-butenes were found to be formed by DBM of 1-butene on D-ZSM-5. The ratio of the amount of the produced 2-butenes in Figure 1e was estimated by using the ratio of the absorption coefficients of C=C stretching bands ($\epsilon_{cis}/\epsilon_{trans} = 2.6$ on D-ZSM-5) as *cis*-/*trans*- = 1.5. To make clear whether each 2-butene was formed by independent paths or one of them was initially produced and was converted to the other, adsorption of *cis*- and *trans*-2-butenes was observed in the heating procedure under evacuation. IR spectra of *cis*- and *trans*-2-butenes in 1:1 π-complex with OD groups of BAS are shown in parts a and c of Figure 6, respectively. Both species showed the same IR spectra at any temperatures below 230 K as those in Figure 6a,c. Above 260 K, the decrease of the integrated intensity of the hydrogen-bonded OD groups resulted from the H/D isotope exchange reaction, which is consistent with the result in Figure 1. The concurrent appearance of a broad band around 1630 cm^{-1} in Figure 6b, indicates the dimerization above 260 K. Either reaction from *trans*- to *cis*- or from *cis*- to *trans*-2-butene was not observed (see bands in the C=C stretching region) below the dimerization temperature. Therefore, the dominant production of either 2-butene followed by transformation to the other cannot account for the formation ratio (*cis*-/*trans*- = 1.5) from 1-butene on BAS of D-ZSM-5 at 230 K (Figure 1d). Hence, there exist individual production paths from 1-butene to *cis*- and *trans*-2-butenes. The absence of the *cis*-/*trans*- isomerization and the occurrence of the dimerization up on H/D isotope exchange reaction may indicate the existence of a stable intermediate (alkoxy species).

Activation Energy for DBM of 1-Butene on D-ZSM-5. The rate of the DBM of 1-butene on D-ZSM-5 was measured by changing the reaction temperature between 218 and 242 K. The concentration of the adsorbed 1-butene at the time *t*, [*x(t)*],
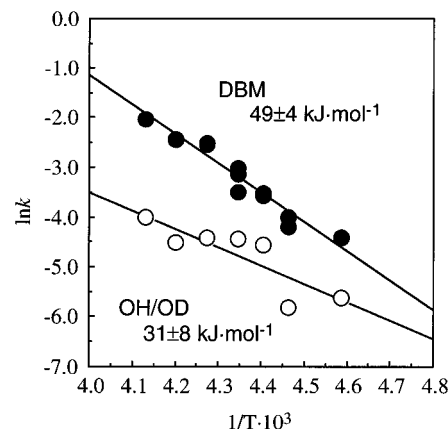

Figure 7. Arrhenius plots for the DBM of 1-butene to 2-butenes and OH/OD isotope exchange reaction on D-ZSM-5.

was represented by the integrated intensity of the C=C stretching band at 1627 cm^{-1} of 1-butene. The rate of the reaction was expressed as follows,

$$r = k[x(t)] = -\frac{d[x(t)]}{dt} \tag{1}$$

$$\frac{[x(t)]}{[x(0)]} = \exp(-kt) \tag{2}$$

where *r* and *k* represent the rate and the rate constant of the reaction. The rate constants were obtained by fitting the rate of the reaction to the eq 2, giving the Arrhenius plot as shown in Figure 7. The activation energy for the DBM of 1-butene on D-ZSM-5 was estimated as 49 ± 4 kJ·mol^{-1}. The slow H/D isotope exchange reaction of BAS was concurrently observed although the rate of the reaction was much smaller than that of the DBM. This suggests the slight contribution of DBM via the protonated intermediate.
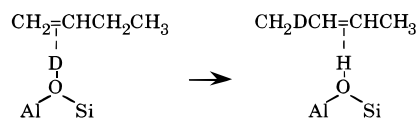
By measurement of the integrated intensity of the hydrogen-bonded OD band at the same time, the rate constants for the H/D isotope exchange reaction at various temperatures were obtained by fitting to the exponential decay. The integrated intensity of the hydrogen-bonded OD band was normalized by the ratios of the absorption coefficients of those of 1-, *cis*-2-, and *trans*-2-butene adsorption systems. The Arrhenius plot for the H/D isotope exchange reaction is also presented in Figure 7. The activation energy was obtained as 31 ± 8 kJ·mol^{-1}, which is smaller than that of DBM in the same temperature range, and the H/D isotope exchange reaction seems to occur in parallel with the DBM. However, it must be recalled that the *cis*-/*trans*- isomerization of the adsorbed butene was not observed at the temperature range (Figure 6), and the alkoxy intermediate was supposed to be stable. If the 2-butene was assumed to be formed from the 1-butene at the H/D isotope exchange reaction in the temperature range of the measurement of the activation energy (between 218 and 242 K), *cis*-/*trans*-isomerization of the adsorbed 2-butene should also proceed at the same temperatures, which was not observed. Therefore, contribution of the DBM accompanied by the protonation from the BAS can be disregarded. The H/D isotope exchange reaction of BAS would occur rather with the formed 2-butene as mentioned above.
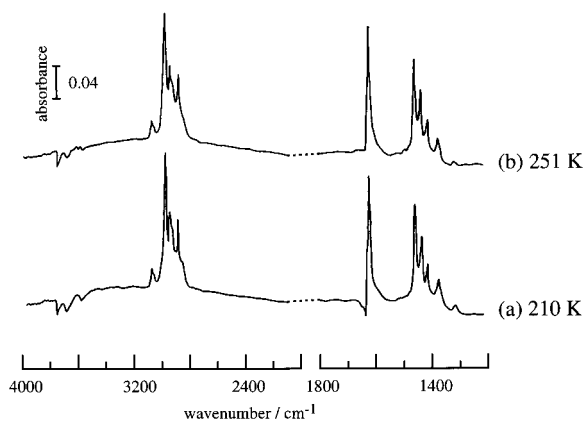
Figure 8. IR spectra of 1-butene adsorbed on Na-ZSM-5 at 210 K (a) and 251 K (b).

Adsorption of 1-Butene on Na-ZSM-5. The present DBM on D-ZSM-5 is strongly suggested to proceed via an intramolecular hydrogen-transfer mechanism, as shown above. The intramolecular hydrogen transfer is also regarded as the mechanism of DBM of 1-butene on basic catalysts,[20-23] where π-allylic carbanion intermediate formed by abstraction of H^{+} is assumed. In these cases, a value more than unity for the product ratio of *cis-/trans*-2-butene from 1-butene was obtained. By comparing the results of the DBM on H(D)-ZSM-5 obtained in the present study with those on basic catalysts, the mechanism of DBM on H(D)-ZSM-5 seems as if some basic sites were responsible on an acidic catalyst. The most probable basicity source is contaminated Na ions exchanged with H. Therefore, the adsorption of 1-butene on Na-ZSM-5 was conducted in the same manner.

IR spectra of adsorbed 1-butene on Na-ZSM-5 at 210 and 251 K are shown in Figure 8. Obviously from the spectra, only the adsorption of 1-butene was observed. Although the temperature was increased to 275 K, the adsorbed 1-butene simply desorbed, and the DBM was not observed. Similar results were obtained by Busca et al., who observed an IR spectrum of 1-butene on Na-Y zeolite at 230 K as well as those on SiO$_2$ at 200 K and TiO$_2$ at 300 K.[24] The adsorption of olefins on alkaline-exchanged zeolites is known to take place on coordinatively unsaturated alkaline ions.[24] These sites were, however, found not capable for any reactions of 1-butene below room temperature.

The inactivity of Na-ZSM-5 for DBM of 1-butene indicates that the DBM on H(D)-ZSM-5 is not due to a possibly contaminated alkaline ions.

Adsorption and DBM of 1-Butene on MOR and FAU. The DBM of 1-butene on D-ZSM-5 was indicated to proceed without proton transfer from the zeolite. To clarify the driving forces of the reaction, two factors of zeolites are varied; the pore size and the acid strength. The former may bring the secondary interaction of the adsorbed molecules with lattice oxygens when it is small as ZSM-5, and the latter may suggest the roll of strong BAS. For the purpose, deuterated mordenite (DM20) and zeolite Y (DY5.6 and DY 4.8) were selected.

Mordenite shows equally strong or stronger Brønsted acidity than that of ZSM-5 and possesses the main channel (0.65 nm × 0.70 nm) and the side channel (0.37 nm × 0.48 nm).[7] The pore size of the former is larger than that of ZSM-5 (0.53 nm × 0.56 nm along the [010] direction or 0.51 nm × 0.55 nm from the [100] direction).[7] Therefore, the secondary interaction of the adsorbed 1-butene with a lattice oxygen, if it exists, would be avoided by employing the larger pore as a field of the
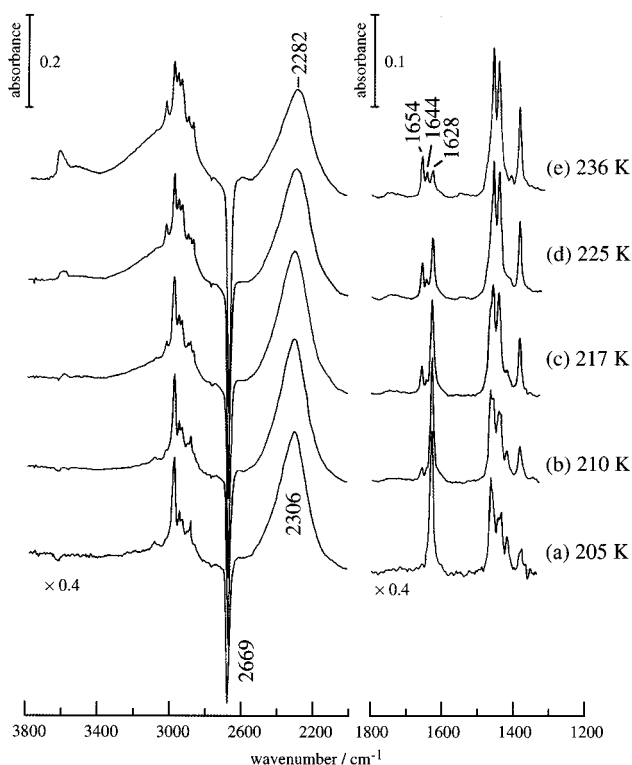
Figure 9. IR spectra of 1-butene adsorbed on DM-20 at 205 K (a) and its thermal change at 210 K (b), 217 K (c), 225 K (d), and 236 K (e).

reaction. The temperature-dependent IR spectra of the adsorbed 1-butene were measured in the same method as that for D-ZSM-5 (Figure 1) as shown in Figure 9. In the case of DM20, weakly adsorbed 1-butene (C=C stretching at 1641 cm^{-1}) was not observed at 205 K, probably due to the larger pore size, which facilitated the direct interaction of 1-butene with BAS. Although two IR bands of OD groups of DM20, one for OD groups in the main channels and the other in the side channels,[12] were overlapped in the background spectrum, it was found that only the main channels provided the adsorption sites of N$_2$ and O$_2$.[12,13] A reverse band at 2669 cm^{-1} observed in Figure 9 is sharper than the original OH band at 2669 cm^{-1}, which indicates that only the acidic OD groups in the main channels were involved in the adsorption of 1-butene. Only ca. 25% of the isolated OD groups in the main channels was occupied by 1-butene (Figure 9b) when ca. 16.0 μmol of the 1-butene was introduced, because the DM20 sample has many more acidic OD groups than the D-ZSM-5 sample has. When the temperature was increased, the similar change of IR spectra to those observed for D-ZSM-5 was observed: (1) C=C stretching band of 1-butene at 1628 cm^{-1} decreased accompanied by the appearance and increase of those bands at 1644 and 1654 cm^{-1}, (2) the spectral features in CH stretching and in 1400-1600 cm^{-1} regions altered, (3) the broad band of the hydrogen-bonded OD groups shifted from 2306 to 2282 cm^{-1}, and (4) the H/D exchange reaction of most of the acidic OD groups was not observed. These clearly indicate that the DBM occurred on DM20 without proton transfer from OD groups to the adsorbed 1-butene. Thus, the secondary interaction of the adsorbed molecules with the lattice oxygens was excluded from the cause of the reaction.

The activation energy of the DBM on DM20 was estimated from 214 to 230 K as 38 ± 8 kJ·mol^{-1}, using the rate of the decrease of the band at 1628 cm^{-1} due to 1-butene. This activation energy is smaller than that of the D-ZSM-5.
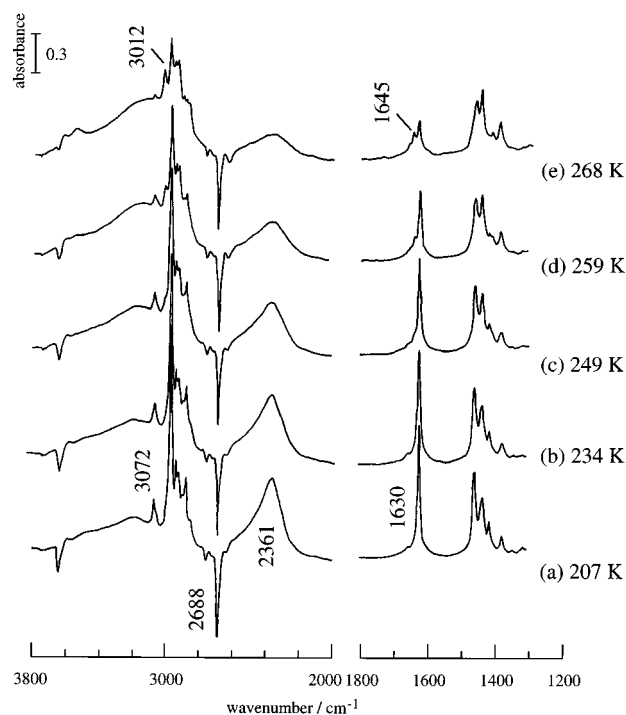
Figure 10. IR spectra of 1-butene adsorbed on DY5.6 at 207 K (a) and its thermal change at 234 K (b), 249 K (c), 259 K (d), and 268 K (e).

The molar ratio of the produced *cis-/trans-*2-butene was estimated as 0.1 by the same method as described above, using the ratio of the absorption coefficients of 2-butenes ($\epsilon_{cis}/\epsilon_{trans}$ = 3.1 on DM20). The difference of the molar ratio of the *cis-/trans-*2-butene on D-ZSM-5 (1.5) and DM20 (0.1) may be attributed to either the acid strength, activation energy, or the structure of the framework; its origin is not clear so far.

The adsorption and reaction of 1-butene on a FAU zeolite, HY5.6, was studied to clarify whether the DBM without proton transfer from zeolites takes place on weaker BAS. A series of IR spectra was measured under the same conditions as that in Figure 1 (Figure 10). There exist two types of acidic OH groups in FAU zeolites: one in α cages (open aperture 7.4 Å) and the other in sodalite cages (open aperture 2.6 Å).[25,26] Their OH (OD) stretching bands appear at 3644 (2691) cm^{-1} (the so-called HF band) and 3555 (2624) cm^{-1} (the LF band), respectively. Only the HF OD groups were found to participate in the adsorption of 1-butene as noticed by a reverse band in Figure 10; a similar result was already demonstrated by our previous study on the adsorption of N$_2$, O$_2$, and rare gases on HY5.6 zeolite.[26] The smaller shift of the HF OD stretching band of the DY5.6 from the isolated to the hydrogen-bonded one ($\Delta\nu$ = −327 cm^{-1}), adsorption of 1-butene on DY5.6 (Figure 10a), was considered to be weaker than that on D-ZSM-5 ($\Delta\nu$ = −369 cm^{-1}) or on DM20($\Delta\nu$ = −363 cm^{-1}) due to weaker acidity. Although the DBM was gradually observed from 234 to 268 K, the concurrent decrease of the hydrogen-bonded OD groups was observed in the same temperature range. The same results as those in Figure 10 were obtained by using another FAU zeolite with a different Si/Al ratio (DY4.8). 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 OH groups of zeolites. The mechanism of the DBM on zeolites with weaker

BAS may be dominated by the proton-transfer one as usually suggested on acidic catalysts,[4,6,9,10] or both reaction paths may proceed simultaneously.

The DBM without proton addition from zeolites was clearly distinguished on strongly acidic MOR (DM20) and ZSM-5 (D-ZSM-5) from that via the proton-transferred intermediate from BAS. The DBM of 1-butene observed in the present study may possibly work in parallel with the conventionally understood mechanism even around room temperature.

4. Summary

The DBM of 1-butene to 2-butene was found by IR to proceed in the absence of the proton transfer from the acidic OH (OD) groups of zeolites below 230 K. The reaction was clearly distinguished on strongly acidic BAS of zeolites (ZSM-5 and MOR) from the H/D isotope exchange reaction of the OH (OD) groups of BAS, which was expected to occur if the alkoxy or carbenium intermediate was assumed. Such a novel reaction route was not differentiated from the alkoxy or carbenium-mediated mechanism on weakly acidic BAS of FAU zeolites. 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 similar mechanisms might simultaneously proceed during the acid-catalyzed reactions in solution.

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