Catalysis Letters 53 (1998) 215–220

IR study of reaction of 2-butene adsorbed on deuterated ZSM-5 and mordenite

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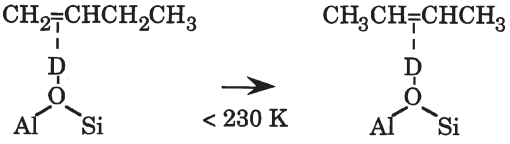
Received 30 January 1998; accepted 26 May 1998

Reactions of *cis*- and *trans*-2-butene adsorbed on deuterated ZSM-5 and mordenite were studied by IR spectroscopy below 300 K. 2-butene molecules hydrogen-bonding to Brønsted acid sites (OD) reacted when the temperature was increased above 250 and 230 K on D-ZSM-5 and D-mordenite, respectively. H/D isotope exchange reaction of Brønsted acidic hydroxy groups accompanied the isomerization of *cis*- to *trans*-2-butene, and then dimerization of *trans*-2-butene followed on ZSM-5, while rapid formation of paraffinic alkoxy groups was dominantly observed on mordenite.

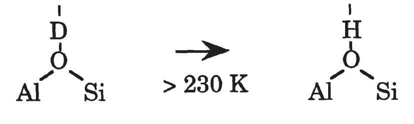
Keywords: FT-IR, adsorption, butene, ZSM-5, mordenite

1. Introduction

We have demonstrated a novel route of double bond migration of 1-butene to 2-butene on strong Brønsted acid sites of zeolites, where proton transfer from Brønsted acid sites to the adsorbed 1-butene molecules was absent [1,2].



Both *cis*- and *trans*-2-butenes were formed by this reaction without the isomerization between the two 2-butenes below 230 K [2]. Above 230 K, where the double bond migration of 1-butene was completed, H/D isotope exchange reaction of Brønsted acid sites was observed, which was suggested to be attributed to the reaction of Brønsted acid sites with the formed 2-butene [2].



In this study, details of the H/D isotope exchange reaction of Brønsted acid sites and *cis*/*trans* isomerization of 2-butene adsorbed on Brønsted acid sites are examined using deuterated ZSM-5 and mordenite by IR spectroscopy. Mobility of 2-butene and stability of the intermediate are also discussed.

2. Experimental

The H-ZSM-5 zeolite (Si/Al = 50) was supplied by Sumitomo Chemical Co., Ltd., and a H-mordenite (HM-20, Si/Al = 10) was offered by Catalysis Society of Japan. A thin disk of the zeolite (ca. 15–25 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 [3] and H(D)-mordenite [4] were treated under the condition that no Lewis acid sites were produced. Each zeolite was deuterated with D_2 at 673 K for 1 h and evacuated at the same temperature. The IR cell was then cooled to ca. 150 K under evacuation while measuring background spectra at several temperatures. A small amount of 2-butene (1.6 μmol for ZSM-5 and 16.0 μmol for mordenite) was introduced below 160 K in order to control the coverage to less than the number of the Brønsted acidic OD groups. Then the cell was immediately evacuated and gradually heated under evacuation. The temperature (measured from outside the cell) was kept constant during measurement (64 scans, ca. 65 s) and was corrected to the sample temperature by calibration curves made by prior experiments. IR spectra were recorded on a Jasco-7300 FT-IR with a MCT detector at an instrument resolution of 4 cm^{-1}.

3. Results and discussion

3.1. 2-butene on D-ZSM-5

A thermal transformation of IR spectra of *trans*-2-butene adsorbed on D-ZSM-5 under evacuation is shown in figure 1, where ca. 80% of Brønsted acid sites is occupied by the adsorbate. A typical IR spectrum of a π-complex, strongly hydrogen-bonded *trans*-2-butene to Brønsted acid sites (OD), was observed at 215 K, which are identified

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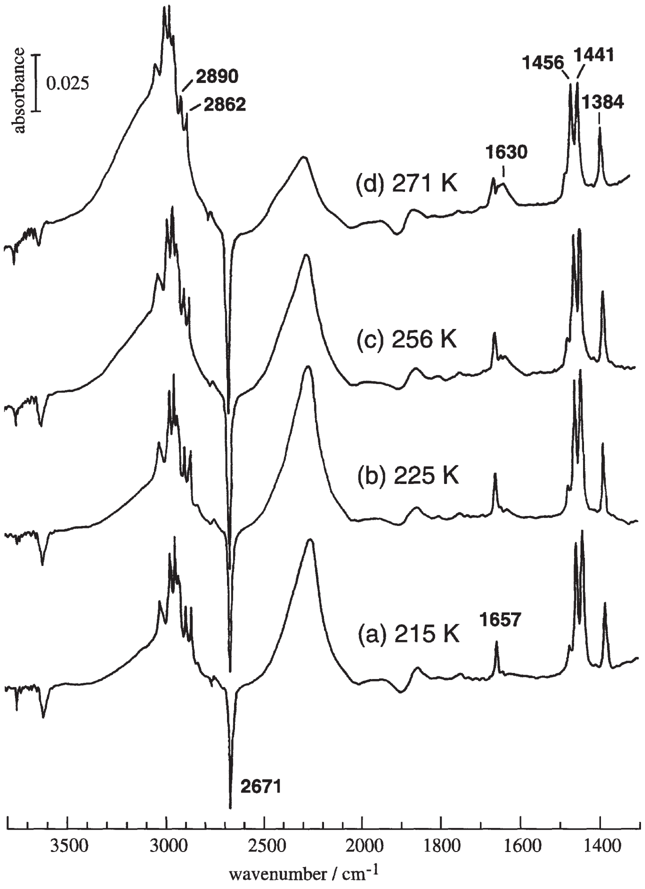


Figure 1. IR spectra of *trans*-2-butene adsorbed on D-ZSM-5 measured during warming procedure under evacuation: (a) 215 K, (b) 225 K, (c) 256 K and (d) 271 K.

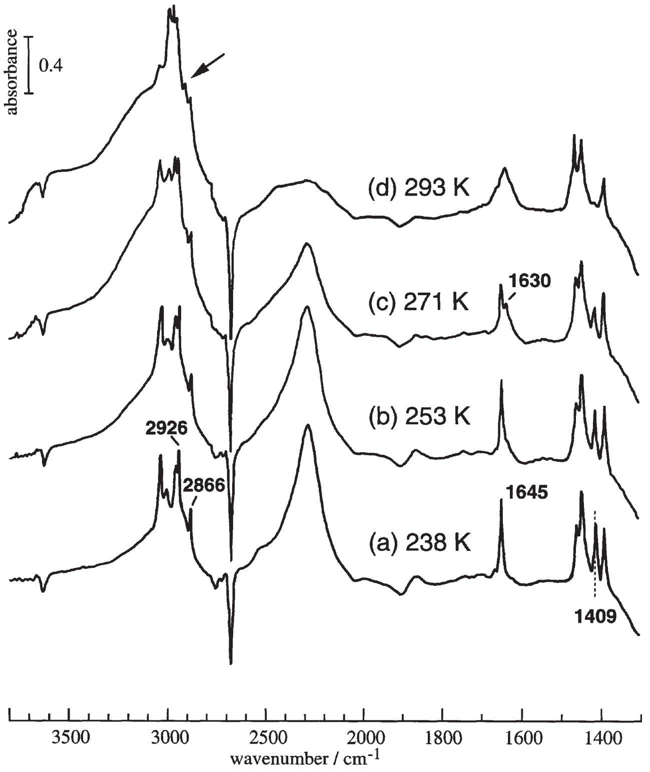


Figure 2. IR spectra of *cis*-2-butene adsorbed on D-ZSM-5 measured during warming procedure under evacuation: (a) 238 K, (b) 253 K, (c) 271 K and (d) 293 K.

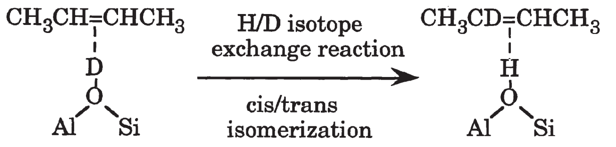
by a decrease of the isolated OD band (2671 cm^{-1}) and the increase of the hydrogen-bonded one (ca. 2260 cm^{-1}), as well as the appearance of a perturbed C=C stretching band of *trans*-2-butene (1658 cm^{-1}, IR inactive mode) at 1657 cm^{-1} [1,2]. A small amount of hydrogen-bonded OH band (ca. 3100 cm^{-1}) was also observed due to Brønsted acidic OH group remaining after deuteration. By increasing the temperature to 271 K under evacuation, decrease of the bands due to π-complex of *trans*-2-butene and Brønsted acid sites (C=C stretching band at 1658 cm^{-1} and the hydrogen-bonded OD band) was observed (figure 1(d)) simultaneously with the change of the spectral appearance in C=C stretching regions (1700–1600 cm^{-1}). The increase of the hydrogen-bonded OH band at ca. 3100 cm^{-1} was also accompanied. The concurrent decrease of the OD band and increase of the OH one indicate the occurrence of the H/D isotope exchange reaction. Alternatively appeared new band at 1630 cm^{-1} is assigned to the dimeric species [5] which have a weak hydrogen-bonding between their alkyl groups and the acidic OH groups (ca. 3500 cm^{-1}). It is noted that the major part of the formed OH groups still had the strong hydrogen-bonding with C=C bond, judging from the OH stretching frequency (ca. 3100 cm^{-1}). Therefore, the H/D isotope exchange reaction of hydrogen-bonded Brønsted acid sites was followed by dimerization at slightly higher temperature range.

Under the present experimental conditions, each *trans*-2-butene molecule was stabilized on a Brønsted acid site forming hydrogen-bonding, and thus, the occurrence of dimerization indicates that the adsorbed butene molecules are already mobile on ZSM-5 [5]. Dimeric species (1630 cm^{-1}) and the isotope-exchanged 2-butene ($CH_3CD{=}CHCH_3$) were observed in the same spectrum in figure 1(d); the latter confirmed by the existence of the isotope-exchanged and hydrogen-bonded OH band at ca. 3100 cm^{-1}. *cis*-2-butene hydrogen-bonded to BAS shows an IR spectrum as observed in figure 2(a). The characteristic bands which distinguish *cis*-2-butene from *trans*-2-butene are the C=C stretching bands at 1645 cm^{-1} and a deformation band at 1409 cm^{-1}. Neither bands were clearly observed in spectrum (d) in figure 1, and therefore, isomerization of *trans*- to *cis*-2-butene was not evidenced. The equilibrium molar ratio (in %) of 1-butene and *cis*- and *trans*-2-butene at 293 K is as follows [6]:

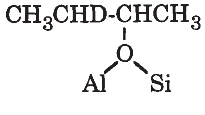
$$\text{1-butene} : \textit{cis}\text{-2-butene} : \textit{trans}\text{-2-butene} = 2.7 : 22.7 : 74.6.$$

From these values, only less than one fourth of *cis*-2-butene is to be formed from *trans*-2-butene, even when the equilibrium is established at 293 K, which seems to be the cause of the lack of observation of *cis*-2-butene formed from *trans*-2-butene.

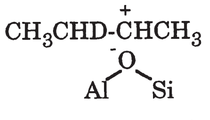
IR spectra of *cis*-2-butene adsorbed on D-ZSM-5 were measured by the same procedure as that in figure 1 and are shown in figure 2. At 238 K, the π-complex of *cis*-2-butene and Brønsted acidic OD groups was noticed by a broad hydrogen-bonded OD band at ca. 2260 cm^{-1} and the C=C stretching band of *cis*-2-butene at 1645 cm^{-1} [8]. All the observed bands at 238 K are attributed to the π-complex of *cis*-2-butene and Brønsted acid sites, and the detailed assignments of other bands have been shown elsewhere [2]. When temperature was gradually increased under evacuation, spectral change was observed similarly to that of *trans*-2-butene. The hydrogen-bonded OD and OH bands decreased and increased, respectively, at the same temperature range (figure 2 (c) and (d)), which was followed by dimer formation (ca. 3500 and 1630 cm^{-1}). *cis*/*trans* isomerization was confirmed by comparison of spectra of *cis*- and *trans*-2-butenes. In the case of *trans*-2-butene, a CH stretching or an overtone of CH$_3$ deformation band at 2890 cm^{-1} was used to infer the existence of *trans*-2-butene, which is absent in a spectrum of *cis*-2-butene (see figure 2(a)). The 2890 cm^{-1} band became observable by heating the sample to 271 K and evident at 293 K, as indicated by an arrow. This confirms the existence of isomerization from *cis*- to *trans*-2-butene during H/D isotope exchange reaction and indicates the same intermediates for both reaction.



The IR spectra of the reaction products of both *trans*- and *cis*-2-butene on D-ZSM-5 appeared almost the same (figures 1(d) and 2(d)). The reaction products include CH/CD isotope-exchanged *trans*-2-butene and dimeric species. The contribution of the former to the IR spectra of the products (figures 1(d) and 2(d)) is regarded as being small, since the characteristic bands of *trans*-2-butene (olefinic CH and C=C stretching) are only slightly observable. On the other hand, dimeric species (1630 cm^{-1}) show their deformation vibrations at 1478 (strong intensity), 1458 (shoulder) and 1385 cm^{-1} (medium intensity) as well as a weakly hydrogen-bonded OH band at ca. 3500 cm^{-1} [5]. Therefore, the dimeric species are not regarded as dominant species which are observed in figures 1(d) and 2(d). These results imply the involvement of stable intermediates for isomerization and hydrogen exchange reaction of *trans*-2-butene, or dimerization in the observed IR spectra. For both H/D isotope exchange reaction and *cis*/*trans* isomerization, a common intermediate, either alkoxy species or carbenium cation, is likely.



alkoxyl species



carbenium species

Results from theoretical calculations on intermediates proposed the stable intermediate of the reaction of olefins with Brønsted acid sites as alkoxy species rather than carbenium cations and suggested that carbenium cations were the transition states [7,8]. Broad IR absorptions of CH stretching bands of carbenium cations in SbF$_5$ solvent were observed between 3100 and 2500 cm^{-1} with their peak maxima at 2830–2730 cm^{-1} [9]. The presently observed IR spectra in figures 1(d) and 2(d) are not regarded as analogous to those of carbenium ions, and alkoxyl species is likely to be included in the spectra. Although any clear spectra of the 2-butoxy intermediate were not obtained due to the coexistence of *trans*-2-butene and dimeric species, the spectral appearance is not largely disapproving to 2-butoxy species. The deficiency in the isolation of IR spectra attributed to 2-butoxy intermediate is due to the successive dimerization arising from the mobility of the adsorbate, as shown below.

3.2. trans-2-butene on D-ZSM-5 at low coverage

For discussion on the mobility of 2-butene, a similar experiment was conducted with much smaller amount of adsorption. The OH and OD stretching region of an IR spectrum of D-ZSM-5 measured under evacuation (before adsorption) is shown in figure 3(a). On the left-hand side as-

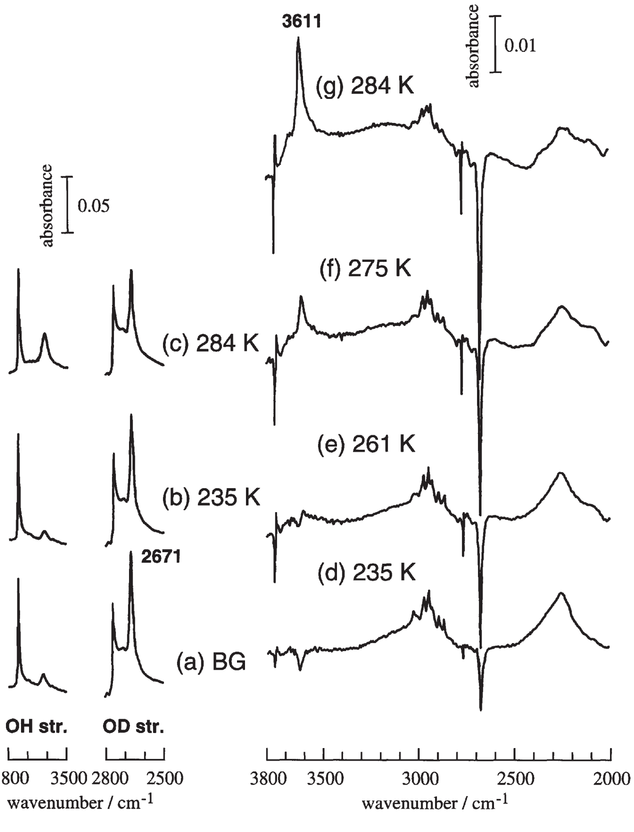
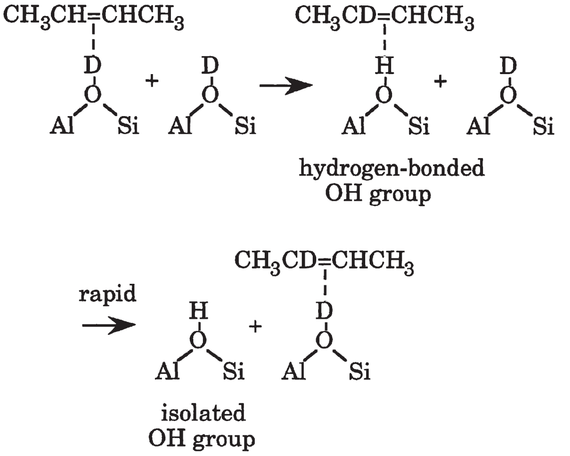


Figure 3. IR spectra of small amount of *trans*-2-butene adsorbed on D-ZSM-5 measured during warming procedure under evacuation. As-observed spectra (a) before introduction of *trans*-2-butene at 235 K, (b) after introduction of 2-butene at 235 K and (c) heated to 284 K. Change of surface species by heating the *trans*-2-butene-adsorbed D-ZSM-5 at (d) 235 K, (e) 261 K, (f) 274 K and (g) 284 K.

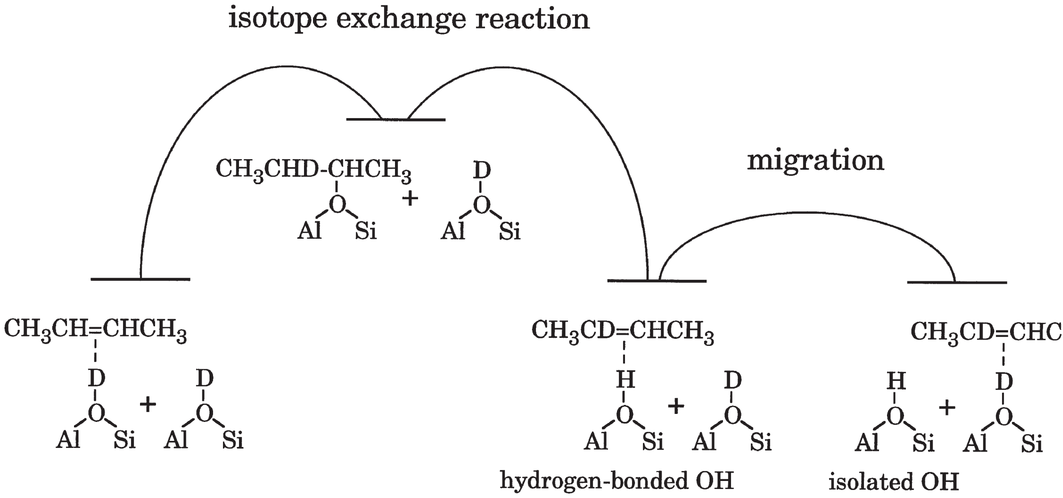
observed spectra are shown, while subtracted spectra of the background (figure 3(a)) are demonstrated on the right-hand side. After introduction and evacuation of *trans*-2-butene on D-ZSM-5 at 235 K, ca. 15% of Brønsted acid sites (both OD and OH) decreased (figure 3(b)) as observed as negative bands in a subtracted spectrum (d). The absorption range below 2000 cm^{-1} is not shown in the subtracted spectra because of "false" bands [10] of zeolites considerably observed due to the expansion of spectra at the low coverage. The hydrogen-bonded OD band slightly decreased in intensity by increasing temperature under evacuation as a result of isotope exchange reaction, but still existed even at 284 K. The band of the produced OH groups was observed as an isolated one which became evident at 284 K. This greatly differs from the results in figures 1 and 2 and indicates the high mobility of 2-butene at the temperature, where proton exchange occurs.



From the result in figure 3, the activation energy for migration is regarded as smaller than that of the isotope exchange reaction or alkoxy formation (31 ± 8 kJ mol^{-1} [2]), as illustrated in scheme 1. The migration of 2-butene observed in this study is considered to be mediated by interaction with the wall of zeolite and the interaction between the alkyl group of butene and Brønsted acidic OD (OH) groups, both of which were observed below 200 K as precursors of the π-complex [11]. The rapid migration of 2-butene molecules is regarded as a cause of the rapid dimerization when the butene coverage was higher, as observed in figures 1 and 2.

3.3. 2-butene on D-mordenite

The effect of the pore size of zeolites on the reactions of 2-butene was studied by using D-mordenite, which possesses the same or higher acidity and larger pore size than D-ZSM-5. *trans*-2-butene was dosed and evacuated below 160 K followed by increasing temperature. The coverage of both *cis*- and *trans*-2-butene (figures 5 and 4, respectively) was less than 20% of the number of Brønsted acidic OD groups. *trans*-2-butene hydrogen-bonded to Brønsted acid sites was observed at 194 K, as shown in the IR spectrum in figure 4(a): the C=C stretching band appeared at 1656 cm^{-1}, which is originally IR inactive, and a broad hydrogen-bonded OD at ca. 2250 cm^{-1}. The H/D isotope exchange reaction was recognized by decrease of the OD band at 254 K, and the formed OH bands were observed at ca. 3100 and 3400 cm^{-1}, while only the former was initially observed on D-ZSM-5. At the same temperature, decrease of the amount of adsorbed *trans*-2-butene was observed (see olefinic CH and C=C bands). The higher reactivities for H/D exchange and for consumption of the adsorbed 2-butene were observed more extensively on D-mordenite than on D-ZSM-5, comparing the spectra in figures 1(d) and 4(d), both measured at similar temperatures. When most part of the hydrogen-bonded OD band was exchanged to OH, the dominant OH band appeared at ca. 3400 cm^{-1}, indicating that a major part of OH groups is not included in the π-complex but weakly hydrogen-bonded with alkyl groups [11,12]. The absence of the OH groups in the π-complex, the first prod-



Scheme 1. Proposed energy diagram for isotope exchange reaction and migration of 2-butene on D-ZSM-5.

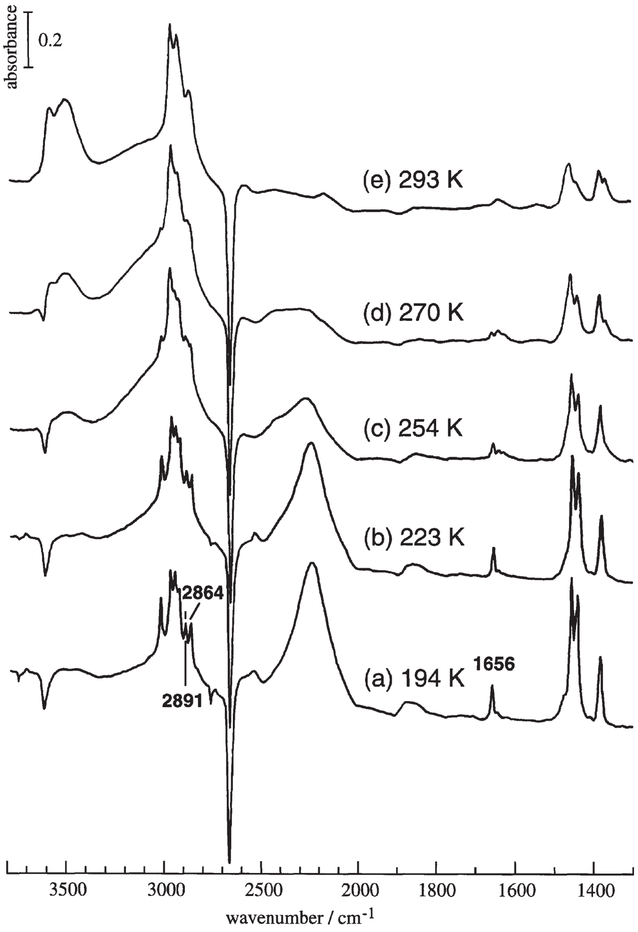


Figure 4. IR spectra of *trans*-2-butene adsorbed on D-MOR measured during warming procedure under evacuation: (a) 194 K, (b) 223 K, (c) 254 K, (d) 270 K and (e) 293 K.

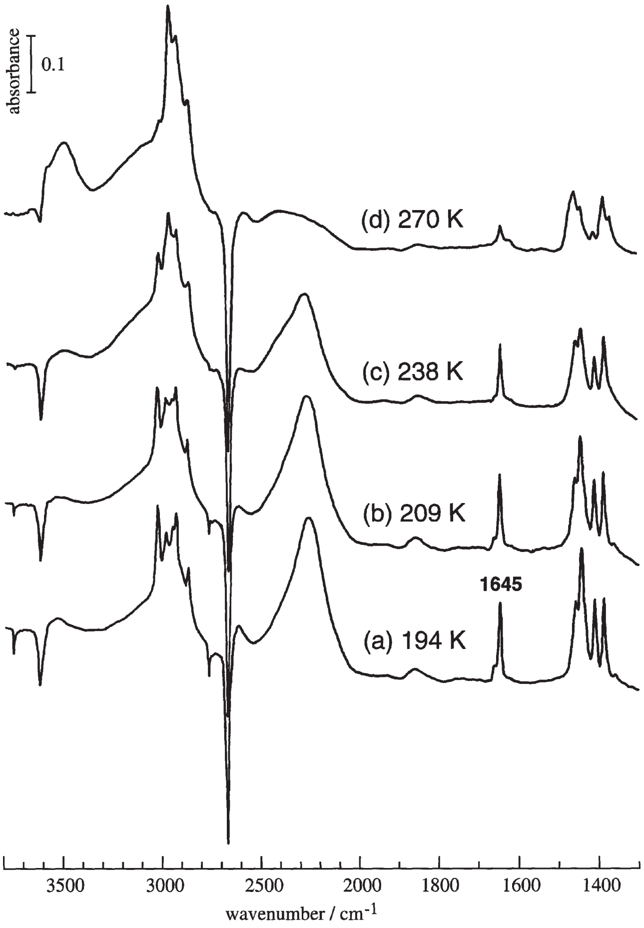


Figure 5. IR spectra of *cis*-2-butene adsorbed on D-MOR measured during warming procedure under evacuation: (a) 194 K, (b) 209 K, (c) 238 K and (d) 270 K.

uct of H/D exchange reaction, indicated that the following intermolecular reaction is more rapid on D-mordenite than on D-ZSM-5. The weakly hydrogen-bonded OH bands of Brønsted acid sites were similarly observed during olefin oligomerization [12] or dimerization [5] on ZSM-5. The reaction product on D-ZSM-5 was reported to be olefinic dimer compounds (3,4-dimethyl-3-hexene, $(CH_3)(C_2H_5)C{=}C(CH_3)(C_2H_5)$) with the weak hydrogen-bonding between its alkyl groups and acidic OH, where the C=C bond was inhibited from direct interaction with acid sited due to steric hindrance [5]. On the other hand, it seems to be branched paraffinic alkoxy groups on D-mordenite. The doublet in CH_3 symmetric deformation bands (1400–1300 cm^{-1}) is characteristic for

$$\rangle CH(CH_3)_2 \quad \text{and} \quad -C(CH_3)_3$$

groups [13], and paraffinic character is evidenced by the absence of any C=C stretching bands. The difference of the reaction product is regarded as a result of the different extent of restriction of the reaction field by different pore size; mordenite pores allow more bulky hydrocarbon product.

cis/*trans* isomerization was studied by adsorption of *cis*-2-butene. IR spectra were measured in the same manner as the others. Hydrogen-bonded *cis*-2-butene to Brønsted acid sites observed at 194 K (figure 5(a)) showed a similar IR spectrum to that on D-ZSM-5 (figure 1(a)), which started H/D isotope exchange reaction at 238 K (figure 5(c)). A CH stretching or an overtone of deformation band at 2891 cm^{-1} identical to *trans*-2-butene did not appear during H/D isotope exchange reaction; formed *trans*-2-butene was not clearly observed, although it should exist. Furthermore, there are no indications on the existence of 2-butoxy intermediate in IR spectra of 2-butene during reactions on D-mordenite (figures 4 and 5); the observed spectra are explained by remaining 2-butene and paraffinic alkoxy groups. These results are in good agreement with the rapid intermolecular reaction on D-mordenite and imply that both hydrogen-exchanged or migrating 2-butene and the alkoxy intermediate are immediately consumed for dimerization or oligomerization on D-mordenite, in contrast to that on D-ZSM-5 [14]. Similarly to D-ZSM-5, migration barrier is regarded as smaller than the activation energy for 2-butoxy formation on D-mordenite based on the immediate dimerization or oligomerization on the surface with the coverage of less than 20%.

4. Summary

H/D isotope exchange reaction of Brønsted acid sites with the adsorbed 2-butene was confirmed to proceed in parallel with the isomerization of 2-butene on D-ZSM-5 below 270 K, and the existence of a common alkoxy intermediate was suggested. The adsorbed 2-butene was found to be mobile below the temperature of alkoxy formation, which resulted in successive dimerization. The reaction of 2-butene adsorbed on D-mordenite was found to allow more bulky paraffinic alkoxy species due to smaller restriction of its larger pore size.

Acknowledgement

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

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