IR study of adsorption and reaction of 1-butene on H-ZSM-5

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Adsorption and reaction of 1-butene on H-ZSM-5 were studied by FT-IR spectroscopy. The adsorbed 1-butenes were converted to cis- and trans-2-butenes below 250 K under evacuation, and dimerization of the adsorbed 2-butenes was observed at room temperature. The produced dimer was tentatively assigned to 3,4-dimethyl-3-hexene which hydrogen-bonded to the acidic OH groups with its alkyl chains. Therefore, the reaction terminated at the dimerization since proton transfer from H-ZSM-5 to the dimer did not occur.

Keywords: FT-IR, adsorption, 1-butene, H-ZSM-5

1. Introduction

The adsorption and reaction of olefins on acid sites of zeolites have been investigated by analyses of the reaction products [1–4], infrared (IR) spectroscopy [1,5–8], nuclear magnetic resonance (NMR) [7,9–13], and electron paramagnetic resonance (EPR) [7,14]. H-ZSM-5 is one of the most widely studied zeolites where ethene and propene were found to be oligomerized or polymerized on Brønsted and Lewis acid sites (BAS and LAS) at room temperature [2,3,5–9]. The reactions of ethene and propene are rather limited: oligomerization, polymerization and H/D isotope exchange with the OD groups of BAS. On the other hand, there are a variety of reactions that may occur with butenes because of the existence of several isomers. Reactions of butenes include double-bond migration and skeletal isomerization in addition to oligomerization, polymerization and H/D isotope exchange. The double-bond migration of butenes has been extensively examined on solid acids (ex. SiO_2–Al_2O_3) and solid bases [15,16], and the cis/trans ratio of the 2-butene product from the double-bond migration of 1-butene has been used to determine the acid–base property of the catalysts. However, in the case of zeolites, steric limitation due to the pore sizes, as well as their strong acidity, affects the cis/trans ratio of the produced 2-butenes. The importance of the pore size of zeolites was recently demonstrated by O'Young et al. for skeletal isomerization of *n*-butenes to isobutene [17,18].

In this study, adsorption and reactions of 1-butene on H-ZSM-5 were studied by IR spectroscopy. Reactions were done below room temperature in the absence of the gaseous molecules in order to observe fundamental reaction steps. The structural effect of H-ZSM-5 on reactions of the adsorbed butene is discussed.

2. Experimental

The H-ZSM-5 zeolite (Si/Al = 50) was supplied by Sumitomo Chemical Co. Ltd. A thin disk of the zeolite (ca. 15 mg, 20 mm in diameter) was placed in an IR cell connected to a closed gas-circulation system. The sample disk of H-ZSM-5 was treated under the condition that no LAS were produced [19]. A small amount of 1-butene (ca. 0.1 Torr) was introduced in order to restrict the coverage of adsorbate not to exceed 100% of the OH groups of BAS. Then the cell was immediately evacuated. IR spectra were recorded on a Jasco-7300 FT-IR with a MCT detector. Sixty-four scans were collected for one spectrum at an instrument resolution of 4 cm^{-1}.

3. Results and discussion

3.1. *Adsorption of 1-butene below 250 K*

Reaction of 1-butene on H-ZSM-5 observed by IR spectroscopy below room temperature is shown first. IR spectra of H-ZSM-5 (figure 1) were measured during gradual heating (ca. 6 K min^{-1}) under evacuation after introducing 1-butene at 180 K. A negative band at 3610 cm^{-1} is due to the isolated OH groups of BAS which decreased by 1-butene adsorption. The interaction of the OH groups of BAS with 1-butene gave rise to a broad band centered at ca. 3100 cm^{-1}, attributed to the hydrogen-bonded OH groups. In addition to the OH stretching band, several bands appeared in the CH stretching region, at 1641 and 1627 cm^{-1} (C=C stretching) and in the deformation region between 1300 and 1500 cm^{-1}. All these bands are attributed to adsorbed 1-butene as observed in Ar matrix [20] and on SiO_2, Na-ZSM-5 and TiO_2 [21]. The two C=C stretching bands could be assigned to two different types of adsorbate. The one at 1641 cm^{-1} stayed at the same frequency as that observed

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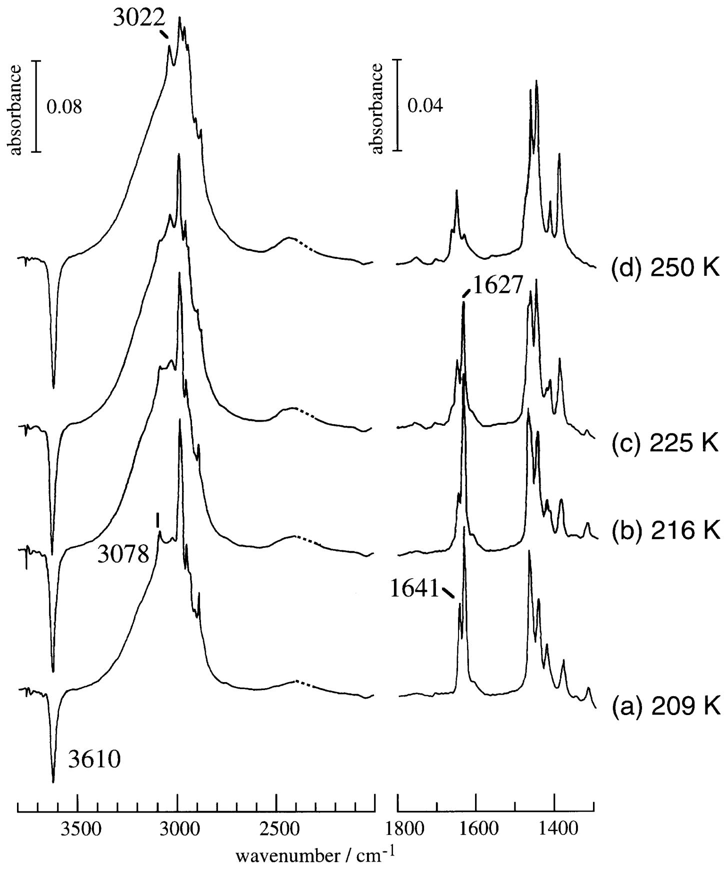
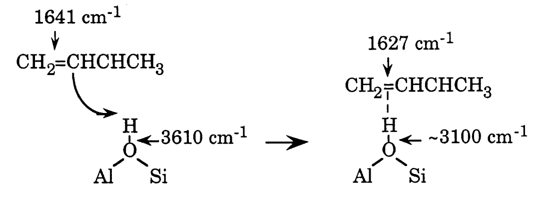


Figure 1. IR spectra of 1-butene adsorbed on H-ZSM-5 measured during warming procedure under evacuation; (a) 209 K, (b) 216 K, (c) 225 K and (d) 250 K.

in Ar matrix [20], and decreased when the temperature was increased to 216 K. This is assigned to a weakly bound adsorbate that does not interact with BAS; that is probably trapped on the framework of H-ZSM-5. (Note that no LAS existed after the pretreatment in the present study.) The other with its C=C stretching band shifted to lower frequency (1627 cm^{-1}) is the hydrogen-bonded species to the OH groups of BAS (ca. 3100 cm^{-1}) in 1 : 1 π-complex as shown below. The integrated intensity of the band at 1627 cm^{-1} observed between 140 and 200 K was plotted vs. the decrease of the isolated OH band of BAS at 3610 cm^{-1} (figure 2). The linear relation indicates the 1 : 1 formation of the BAS and the adsorbed 1-butene with its C=C stretching band at 1627 cm^{-1}. The weakly adsorbed species was dominantly observed at much lower temperature range than that in figure 1 and was found to be converted to the hydrogen-bonded one as the temperature was increased [22].



At 216 K, the decrease of the amount of the adsorbed 1-butene was clearly observed by the decrease of the olefinic CH stretching band at 3078 cm^{-1}, which was accompanied by the appearance of a new band at 3022 cm^{-1}. The change of the spectral feature is also

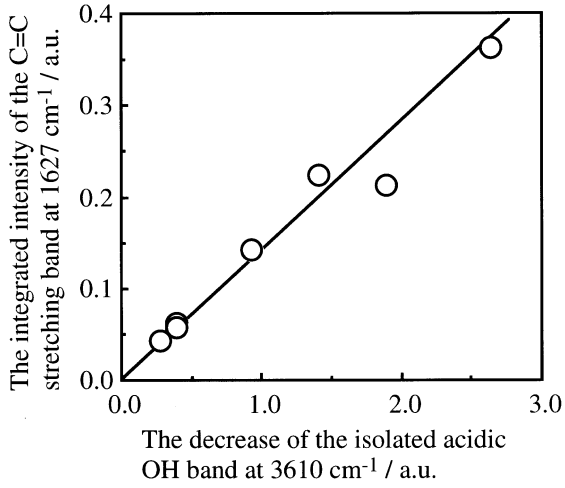


Figure 2. Change of the integrated intensity of the C=C stretching band at 1627 cm^{-1} vs. the decrease of the integrated intensity of the isolated OH groups of BAS at 3610 cm^{-1}.

noted in deformation region between 1300 and 1500 cm^{-1}. The change of the IR spectra became evident when the temperature was further increased. The IR spectrum observed at 250 K completely differed from the one of the adsorbed 1-butene, indicating that a thermal reaction of 1-butene on the BAS of H-ZSM-5 occurred. The preservation of the hydrogen-bonded OH (3100 cm^{-1}) and the olefinic CH (3022 cm^{-1}) and some C=C bands after the reaction evidences the existence of a hydrogen-bonding of the OH groups of BAS with the C=C bond of the reaction products similarly to that with 1-butene.

The most probable candidates for the reaction products of 1-butene on H-ZSM-5 at such low temperatures are regarded as the isomers, cis- and trans-2-butenes. IR spectra of the adsorbed cis- and trans-2-butenes adsorbed on H-ZSM-5 are compared in figure 3 with that of the reaction products (figure 1 (d)). In each spectrum of the adsorbed 2-butenes, a broad band of the hydrogen-bonded OH groups hindered clear observation of CH stretching bands of the adsorbate, which is, therefore, not shown in figure 3. Three intense bands at 1460, 1440 and 1384 cm^{-1} and a C=C stretching band at 1658 cm^{-1} of the reaction products are mainly assigned to the trans-2-butene, and those at 1410 and 1644 cm^{-1} to the cis-2-butene. The C=C stretching band of the free trans-2-butene molecules is IR inactive and was observed by Raman spectroscopy at 1682 cm^{-1} [23].

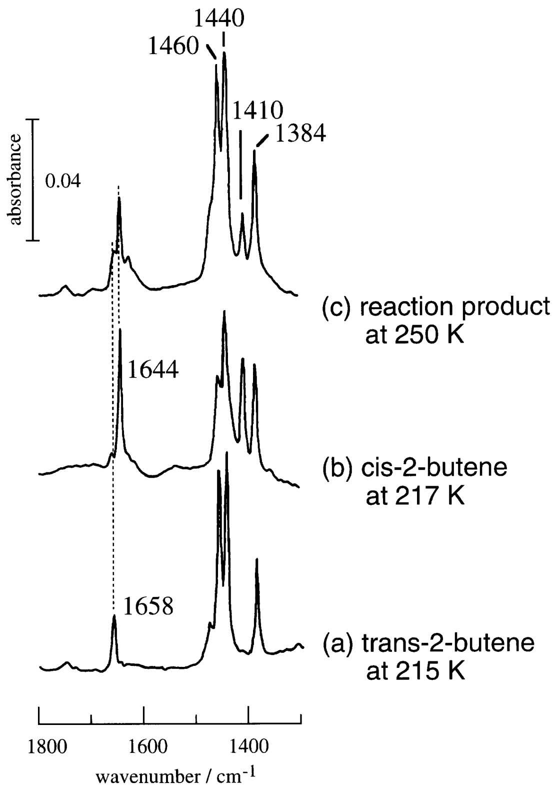
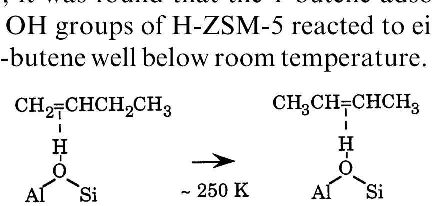


Figure 3. Assignment of the reaction product of 1-butene on H-ZSM-5; IR spectra of (a) trans-2-butene at 217 K, (b) cis-2-butene at 217 K, and (c) the reaction product of 1-butene at 250 K.

Both 2-butenes showed their C=C stretching bands at lower frequency than the free molecules ($\Delta\nu = -23\ cm^{-1}$ for cis- and $-25\ cm^{-1}$ for trans-2-butene), supporting the existence of the hydrogen bonding of the acidic OH groups and the C=C bonds. Therefore, it was found that the 1-butene adsorbed on the acidic OH groups of H-ZSM-5 reacted to either cis- or trans-2-butene well below room temperature.



The detailed and somewhat unusual mechanism of the above reaction is described using isotopes elsewhere [22].

3.2. Adsorption of 1-butene at room temperature

The adsorption and the reaction of 1-butene following to the double-bond migration was studied next at room temperature. The H-ZSM-5 sample was exposed to 0.1 Torr of 1-butene and the system was immediately evacuated. About 80% of the isolated OH groups of BAS were occupied by the adsorbates. The IR spectrum of the adsorbed species formed by 1-butene adsorption at room temperature is shown in figure 4 (a), 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 (figure 4 (b)). The hydrogen-bonded OH groups observed at ca. 3100 cm^{-1} disappeared after 120

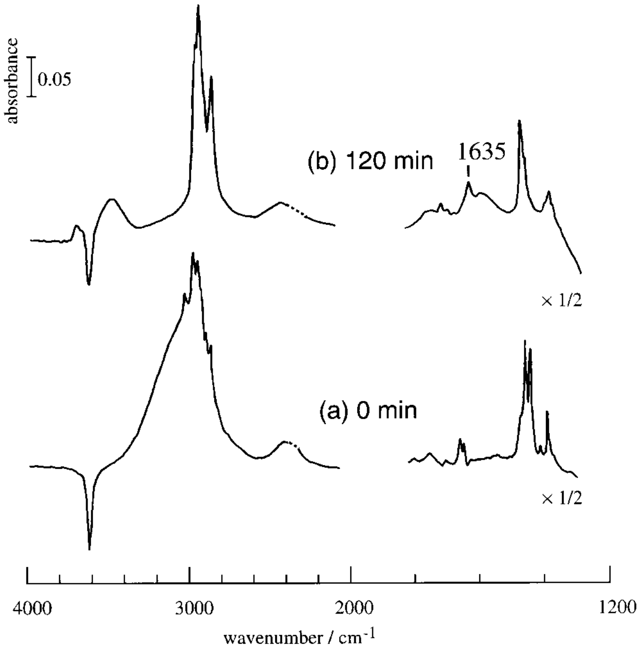


Figure 4. IR spectra of 1-butene adsorbed on H-ZSM-5 at room temperature; (a) soon after the reaction, and (b) 120 min after the reaction started.

min, and a small band at ca. 3500 cm^{-1} appeared. Simultaneously, the negative band due to the isolated OH groups decreased. The bands of the adsorbed species also changed in the CH stretching (2800–3100 cm^{-1}), C=C stretching (1600–1700 cm^{-1}) and deformation (1200–1500 cm^{-1}) regions. The subtracted spectrum of (a) from (b) in figure 4 shown in figure 5 (a) clearly demonstrates the above-mentioned changes in the spectra.

The change of the integrated intensity of the isolated OH band of BAS in the time course of the reaction observed in figures 4 and 5 is described in figure 6. 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 figure 6 may be recovered from hydrogen-bonded ones as a result of the decrease in the amount of the adsorbed butene.

For confirming the reaction as dimerization, additional adsorption of 1-butene was carried out to the H-ZSM-5 observed in figure 4 (b). The change of the spectra, where the spectrum of figure 4 (b) was used as a background, during the reaction for 120 min was almost the same as those in figure 4 except the overall intensity of the absorbance. The subtracted spectrum of the one measured soon after the reaction from that after 120 min is shown in figure 5 (b). Obviously the same spectrum was obtained: the same reaction proceeded on the vacant BAS, and the product of the first reaction independently existed on the H-ZSM-5 surface. The time course of the reaction was also the same in the first and the second runs as plotted in figure 6; about half of the isolated OH groups which was decreased by butene adsorption recovered from the hydrogen-bonded OH groups. If oligomerization or polymerization is assumed to proceed, it would extensively dominate the reaction more in the second run than in the first run, and the series of spectra would result in different way. Therefore, it is concluded that the reaction of the adsorbed butenes terminates at dimerization and that oligomerization or polymerization does not proceed.

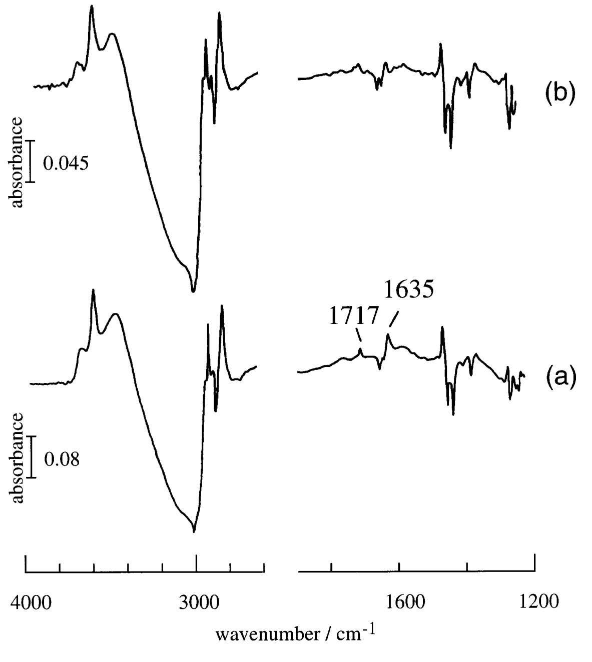


Figure 5. Subtracted IR spectra of the reaction of butene at room temperature, (120 min)/(soon) after the reaction; (a) first adsorption of 1-butene, and (b) second adsorption of 1-butene.

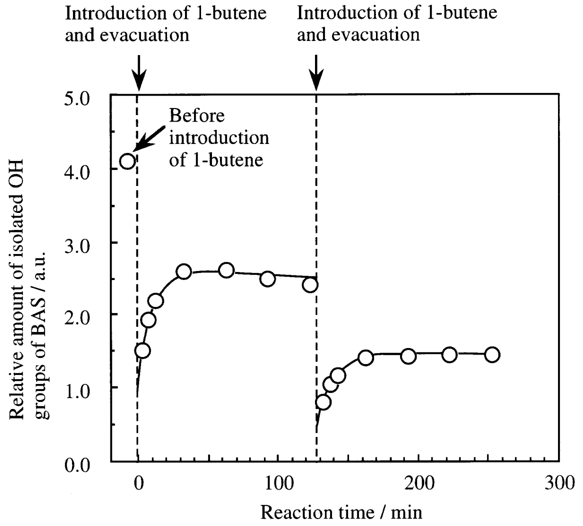
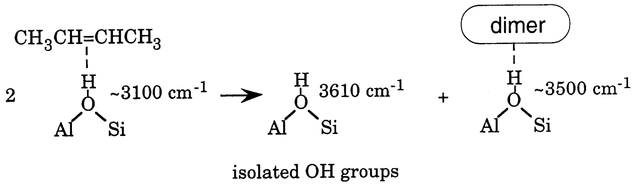
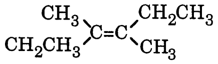


Figure 6. Time course of the integrated intensity of the isolated OH groups of BAS on H-ZSM-5.



The geometrical and adsorption structures of the produced dimer compound are then considered. The characteristics of the IR spectrum (figure 4 (b)) of the adsorbed dimer are as follows: (1) the OH groups hydrogen-bonded with the dimer were observed at around 3500 cm^{-1}, (2) a weak C=C stretching band was observed at 1635 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 was observed when a saturated hydrocarbon (*n*-heptane) adsorbed on H-ZSM-5, which indicated a weak hydrogen-bonding of OH groups of BAS with an alkyl group [8]. The alkyl chains of the oligomer or polymer produced by reaction of ethene and propene on H-ZSM-

5 were found to have such a weak hydrogen-bonding with the OH groups of BAS, by comparison with that of *n*-heptane [8]. In the present study 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 above mentioned consideration, the structure of the dimer is expected to be as follows.



3, 4-dimethyl-3-hexene

Only the trans form is shown for simplicity. This compound would be produced by a reaction of carbenium ion and 2-butene. There are other possible structures for the product of dimerization of 2-butene such as 3,4-dimethyl-2-hexene. However, they would be isomerized to a stable tetra-substituted ethene, 3,4-dimethyl-3-hexene, as a result of double-bond migration on BAS.

The C=C bond of the produced dimer was found to be hindered to hydrogen-bond with the OH groups of BAS due to the steric hindrance. Therefore, protonation of the dimer would not occur, and further reactions such as oligomerization and polymerization would not proceed.

4. Summary

The 1-butene hydrogen-bonded to the acidic OH group of H-ZSM-5 was found to be transformed to hydrogen-bonded 2-butene below 250 K. The reaction of the adsorbed 2-butene ceased at dimerization since the C=C bond of the dimer (tentatively 3,4-dimethyl-3-hexene) was sterically hindered to approach the OH group. The dimer adsorbed on the acidic OH groups via hydrogen-bonding with its alkyl chains.

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