IR study on the reaction path of skeletal isomerization of 1-butene

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The reaction molecularity of the skeletal isomerization on zeolite was deduced from IR spectra of adsorbed butene recorded with heating. Formation of polymeric species from adsorbed butene was observed on ZSM-5 and beta zeolites, non-selective catalysts for isobutene production. On the other hand, most of butene molecules adsorbed on ferrierite and clinoptilolite behaved monomolecularly, resulting in complete desorption even at ambient temperature. The exceptional selectivity for isobutene of ferrierite and clinoptilolite was ascribed to the sparse distribution of adsorbed butene molecules, suppressing bimolecular oligomerization and enhancing monomolecular skeletal isomerization.

Keywords: molecularity, skeletal isomerization, butene, zeolite

1. Introduction

Ferrierite (FER) has attracted great interest due to its exceptional selectivity for isobutene, after a successful commercialization of the skeletal isomerization process of n-butene in 1993 [1]. Although there are several suggestions to explain the exceptional selectivity [1,2], the specific pore structure of FER zeolite composed of 8- and 10-membered rings is considered to be a plausible cause bringing about the selective skeletal isomerization. Since cracking of oligomer formed from n-butene produces various hydrocarbons, the suppression of the bimolecular reaction is essentially required to achieve a high selectivity for isobutene. Therefore, the high preference for the monomolecular reaction path resulting in the pore structure of FER zeolite, is suggested to be the fundamental cause for the exceptional selectivity [2].

However, the high selectivity for isobutene is also obtained on modified alumina catalysts with small loading of fluorine [3] and mesoporous material catalysts with low content of aluminium [4]. Both catalysts have a low concentration of strong acid sites, inducing the suppression of bimolecular oligomerization. Regardless of pore diameter and shape, the sparse distribution of activated n-butene molecules on the catalyst surface suppresses the bimolecular oligomerization and results in the high preference of the monomolecular reaction, achieving the high selectivity for the skeletal isomerization.

Recently, the suggestion of the monomolecular path for the skeletal isomerization has become to be accepted [5,6], even though there are several rebuttals such as a high potential barrier for the formation of unstable intermediate and a low possibility for the complete exclusion of the bimolecular reaction. The weak point of the suggestion is rare evidence for the monomolecular reaction path. The increase in the selectivity with the decrease in the partial pressure of n-butene [7], and the isotope distribution in products of the skeletal isomerization supposed the monomolecular isomerization path [8]. However, a direct observation of the monomolecular proceeding of the skeletal isomerization is not reported.

In this study, IR spectra of various adsorbed olefins on zeolite catalysts were recorded with temperature increase to deduce the reaction molecularity. Four zeolites with different pore structures and acidities were used to elucidate the difference in the reaction molecularity. FER and clinoptilolite (CLI) zeolites were used as selective catalysts [1,2,9], while ZSM-5 (MFI) and beta (BEA) zeolites were used as non-selective catalysts [2]. The difference in the adsorption–desorption behavior of butene molecules on these zeolites was discussed in relation to their selectivities for the skeletal isomerization.

2. Experimental

FER zeolite with Si/Al ratio of 7.5 was synthesized using pyrrolidine as a structure-directing agent described elsewhere [10]. Colloidal silica (Ludox HS 40, Du Pont; 39.5% SiO_2, 0.4% Na_2O, 60.1% H_2O) and sodium aluminate (Stream, GR) were used as silicon and aluminium sources, respectively. CLI zeolite with Si/Al ratio of 6 was synthesized using a seeding technique following a procedure described in the literature [11]. MFI zeolite with a Si/Al ratio of 25 and BEA zeolite with a Si/Al ratio of 13 were obtained from Zeolyst Corporation and PQ Corporation, respectively. These zeolites were converted to H-form by an ammonium ion exchange using a 0.5 N ammonium nitrate solution (Junsei Chemical Co.) followed by calcination at 550 °C.

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The acidity of the catalyst was investigated through the temperature-programmed desorption (TPD) of ammonia [2]. The amount of ammonia desorbed from the sample was determined with a quadropole mass spectrometer (Balzers, QME 200).

The skeletal isomerization of 1-butene was carried out using a conventional continuous-flow microreactor loaded with 0.2 g of zeolite at an atmospheric pressure described elsewhere [9].

The skeletal isomerization of 1-butene was monitored by an FT-IR spectrophotometer (BIO-RAD, FTS175C) with an *in situ* cell made by GRASEBY SPECAC [12]. A self-supported wafer of a 10 mg zeolite was evacuated under vacuum of 0.03 Pa at 550 °C for 30 min and exposed to 30 kPa of 1-butene (Praxair Korea, 99.9%) at 30 °C for 30 min. The catalyst was evacuated at 30 °C for 10 min to remove the physically adsorbed 1-butene. Upon heating to 550 °C with 16 °C min^{-1} under evacuation, IR spectra of adsorbed butene on the zeolite were recorded from a transmitted IR beam through the zeolite. The scan range of the IR spectrum was 1300–4000 cm^{-1} and resolution 4 cm^{-1}. The adsorption–desorption behaviors of n-butane (Matheson, CP), isobutene (Praxair Korea, 99.9%), n-heptane (Aldrich, 99.0%) and 1-heptene (Aldrich, 99.0%) were also examined by the same procedure used for the IR study of 1-butene.

IR spectra of the adsorbed species of 1-butene on the zeolite were also recorded under 1 kPa of 1-butene. Since the gas phase was not evacuated during heating, catalytic reactions were carried out on the zeolite. The gas phase in the cell and adsorbed species on the zeolite were monitored by the IR spectrophotometer, changing the light path according to the object to be measured. The cell was heated up to 450 °C to avoid contamination of the ZnSe windows.

3. Results and discussion

Since the skeletal isomerization of 1-butene to isobutene is an acid-catalyzed reaction, the acidity of the zeolite is regarded as the primary concern for their catalytic properties. TPD profiles of ammonia from four zeolites are shown in figure 1. Two desorption peaks are observed on the pro-
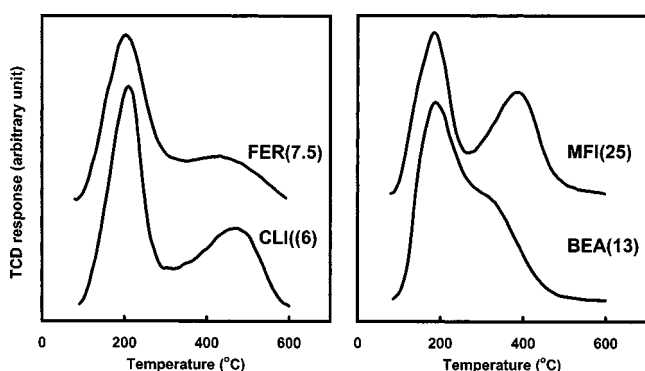
files at temperature ranges of 190–200 and 350–450 °C. Low (l-) and high (h-) temperature peaks can be attributed to ammonia desorbed from weak and strong acid sites, respectively [13]. l-peaks are similar for all zeolites in the aspects of the temperature at peak maximum and peak areas, regardless of their zeolite types and Si/Al molar ratio. The temperatures at h-peak maximum (T_M) of the FER and CLI zeolites are similar to each other, but the area of the h-peak of the FER zeolite is smaller than that of the CLI zeolite. On the other hand, both the area and T_M of the h-peaks are different on the MFI and BEA zeolites. T_M of the MFI zeolite is 410 °C, whereas that of the BEA zeolite is 360 °C. The area of h-peak of the BEA zeolite is considerably small compared to the MFI zeolite.

TPD profiles indicated that the number and strength of strong acid sites of zeolites predominantly depend upon their structures. Although the Si/Al molar ratio must be a factor affecting the number of acid sites, the zeolite structure is more important in determining the number and strength of strong acid sites [13]. The BEA zeolite has the smallest number of strong acid sites among the four zeolites, while the CLI zeolite has the largest. Acid strengths of the MFI and FER zeolites are similar, while the number of strong acid sites of the MFI zeolite is larger than that of the FER zeolite. Therefore, the four zeolites can be ordered as BEA < FER < MFI < CLI for the number of strong acid sites.

The conversion and selectivity of zeolite catalysts in the skeletal isomerization depended considerably on the structure of the zeolite, as well as acidity. Table 1 shows typical conversion and selectivity obtained from the MFI, BEA, FER and CLI zeolites. Although it is more reasonable to compare the selectivity at a constant conversion, the increase in the conversions of the FER and CLI zeolites is impossible due to the low content of isobutene among butene isomers at thermodynamic equilibrium of elevated temperature [5]. Thus, the conversion and selectivity listed in table 1 were obtained under the same reaction conditions for qualitative comparison.

A large amount of various hydrocarbons such as $C_2^=$, C_3, $C_3^=$, C_4 and C_{5+} was formed on the MFI and BEA zeolites, resulting in the low selectivity for isobutene. On the other hand, the high selectivity for isobutene was observed over the FER and CLI zeolites. Since there is no thermodynamic limitation for producing various hydrocarbons, the

Figure 1. Ammonia TPD profiles from FER, CLI, MFI and BEA zeolites.

Table 1
Conversion and product selectivity in the skeletal isomerization of 1-butene over various zeolite catalysts at 450 °C.[a]

Catalyst	Si/Al	Conversion (%)	Selectivity (%)					
			$C_2^=$	C_3	$C_3^=$	n-C_4	i-$C_4^=$	C_{5+}
MFI	25	83.1	35.6	9.8	29.7	6.3	11.6	6.1
BEA	13	27.8	4.7	6.0	29.0	4.6	40.3	15.5
CLI	6	16.0	0.0	0.0	4.8	2.6	89.5	5.1
FER	7.5	37.0	0.7	0.1	6.8	0.8	89.3	2.4

[a] Data reported are the average values at 70 min of time on stream, WHSV = 3.0 h^{-1}.
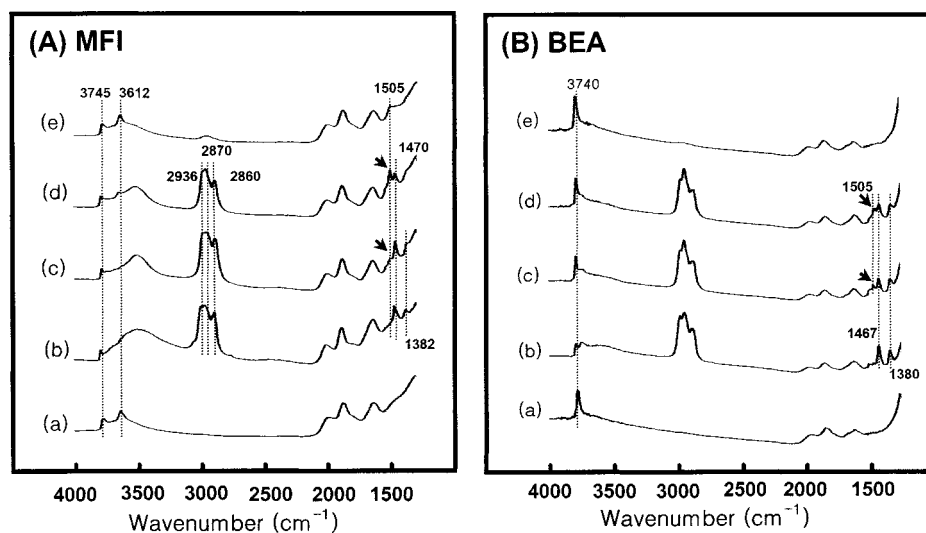
Figure 2. IR spectra of adsorbed 1-butene on MFI (A) and BEA (B) zeolites. Zeolite was evacuated at 550 °C (a), exposed to 1-butene and evacuated at 30 (b), 200 (c), 250 (d) and 450 °C (e) .

non-selective MFI zeolite shows high conversion. The poor conversion and high selectivity for C_{5+} of the BEA zeolite is due to its weak acidity compared to the MFI zeolite, resulting in the slow cracking of oligomers.

The adsorption of 1-butene on a zeolite following its desorption and reaction was investigated using the IR spectrophotometer. Figure 2 shows IR spectra of 1-butene adsorbed on the MFI and BEA zeolites, the non-selective catalysts for isobutene production. The absorption band of an isolated OH group was observed at 3745 cm^{-1} and of an acidic OH group at 3612 cm^{-1} on the MFI zeolite after evacuation at 550 °C (figure 2(A)). The bands at 1970, 1850 and 1620 cm^{-1} are due to framework vibrations of the zeolite. New absorption bands at 2800–3200, 1470 and 1382 cm^{-1} were observed with adsorption of 1-butene. With the appearance of the new bands, the band of the acidic OH group at 3612 cm^{-1} shifted to a lower wavenumber, indicating the interaction between 1-butene and acid site. Upon elevating the evacuation temperature to 200 °C, a new band was observed at 1505 cm^{-1}. The band of 1505 cm^{-1} increased more intensely with heating at 250 °C, accompanying the decrease in the band of 1470 cm^{-1}. A further increase in the evacuation temperature to 450 °C brought about complete desorption of butene and recovery of the original IR spectrum of the evacuated zeolite.

The absorption bands of 1-butene adsorbed on the MFI zeolite were scrupulously assigned by Trombetta et al. [14]. The shoulder band at 3020 cm^{-1} is due to asymmetric CH stretching of olefins and the bands at 2936, 2870 and 2860 cm^{-1} are due to symmetric CH stretching. Asymmetric and symmetric CH$_3$ deformation bands are observed at 1470 and 1382 cm^{-1}, respectively. The 1505 cm^{-1} band observed at the heating treatment was assigned to polymeric species.

The decrease in the acidic OH band of the MFI zeolite with adsorption of 1-butene suggests that 1-butene mol-

ecules are adsorbed on acid sites. The adsorbed butene forms a carbenium ion complex as suggested by Kondo et al. [15]. However, an increase in the band of 1505 cm^{-1} accompanied by the decrease in the band of 1470 cm^{-1} with heating at 200 °C, indicates the formation of polymeric materials from adsorbed butene species in the pore of MFI zeolite.

The formation of polymeric materials was also observed on the BEA zeolite (figure 2(B)). Although there are several differences between the MFI and BEA zeolites, such as the band shape of the OH bond and the strength of acid sites, overall IR spectra for the adsorption–desorption of 1-butene on the BEA zeolite are almost the same as those of the MFI zeolite. The coincidence in the IR spectra of butene species adsorbed on the MFI and BEA zeolites suggests that the adsorption–desorption and reaction behaviors of 1-butene and their products on both zeolites are similar.

The formation of a 1505 cm^{-1} band from adsorbed butene species on the MFI and BEA zeolites by heating is more clearly observed from the sequential 3D IR spectra (figure 3). Although band intensities were weak on the BEA zeolite, the increase in the band of 1505 cm^{-1} accompanied by the decrease of the bands of 1470 and 1382 cm^{-1} is similar on both zeolites.

The formation of polymeric species on the MFI zeolite with adsorption of isobutene and 1-heptene was also observed, as shown in figure 4. There was no significant difference among the olefins, in the aspect of the formation of polymeric species on the MFI zeolite. However, the polymeric species was not formed on the MFI zeolite with adsorption of *n*-butane and *n*-heptane followed by heating with evacuation. The bands of 1470 and 1380 cm^{-1} assigned to a CH bond were observed with the adsorption of *n*-heptane, while they disappeared completely with evacuation at 100 °C. *n*-butane adsorbed on MFI zeolite was desorbed more easily with evacuation even at 30 °C. Furthermore, the band at 1505 cm^{-1}, which indicated the
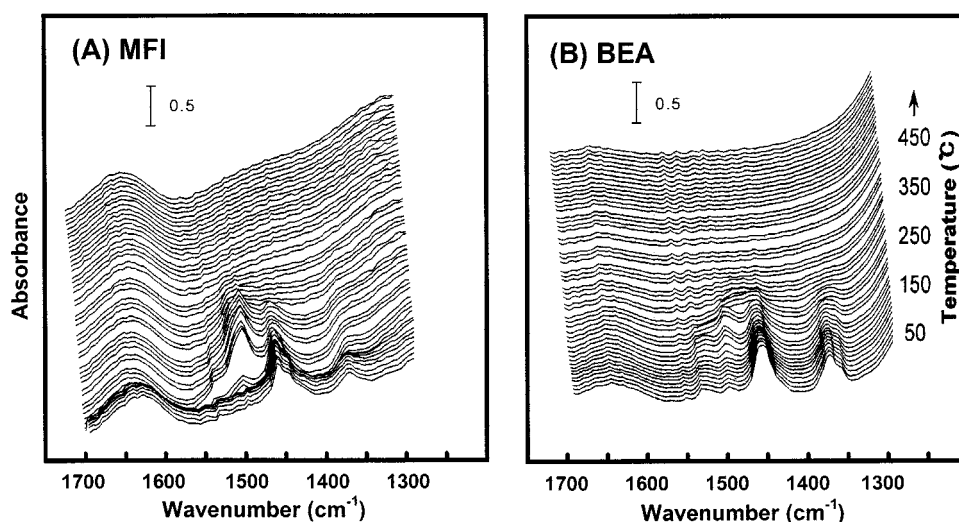
Figure 3. 3D IR spectra of adsorbed 1-butene on MFI (A) and BEA (B) zeolites. Zeolite was exposed to 1-butene at 30 °C and evacuated with temperature increasing to 550 °C with a ramp of 16 °C min^{-1}.
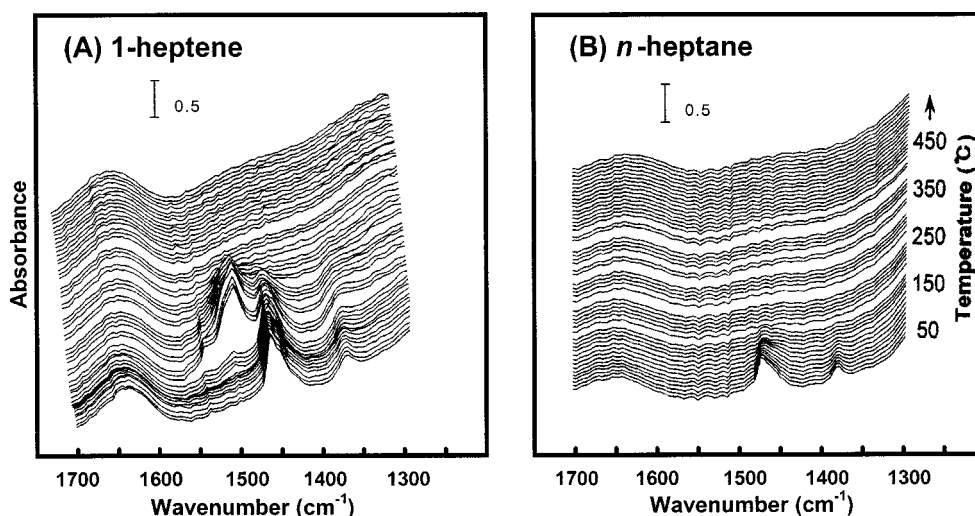

Figure 4. 3D IR spectra of adsorbed hydrocarbon on MFI zeolite. Zeolite was exposed to 1-heptene (A) and n-heptane (B) at 30 °C and evacuated with temperature increasing to 550 °C with a ramp of 16 °C min^{-1}.

formation of polymeric species was not observed with adsorption of saturated hydrocarbons.

The adsorption–desorption behaviors of 1-butene on the FER and CLI zeolites are remarkably different from those on the MFI and BEA zeolites. Absorption bands of 1-butene adsorbed on the FER zeolite were observed after evacuation at room temperature, but they disappeared with evacuation even at slightly elevated temperatures, as shown in figure 5. Adsorbed butene species on the CLI zeolite were completely desorbed with evacuation even at room temperature. Therefore, the band of 1505 cm^{-1}, indicating the formation of polymeric species, was not observed on the FER and CLI zeolites due to fast desorption of butene.

The strength of strong acid sites of the BEA zeolite is weaker than those of the FER and CLI zeolites, but butene species adsorbed on the BEA zeolite are retained after evacuation even at elevated temperatures. Although the FER and CLI zeolites have plenty of strong acid sites, adsorbed

butene is easily desorbed with evacuation even at room temperature. This means that the interaction between the butene molecule and the strong acid site is not the main cause of retaining an adsorbed state of butene species on the MFI and BEA zeolites. The desorption of n-butane, however, is fast both on the MFI and FER zeolite. Therefore, the adsorbed butene species can be retained on the MFI and BEA zeolites with the oligomer formation of higher boiling points. Since the transfer of butene molecules along the pore of MFI zeolites is easy [16], there is no severe restriction to the formation of butene oligomers in the MFI zeolite pore, lowering vapor pressure and retaining the adsorbed state. On the other hand, the transfer of butene molecules along the pore of FER and CLI zeolites is restricted, due to their specific pore shape [7,9]. Monomoleculary adsorbed butene species on the FER and CLI zeolites are easily removed with evacuation as in n-butane, because they do not form any oligomers in the zeolite pore.
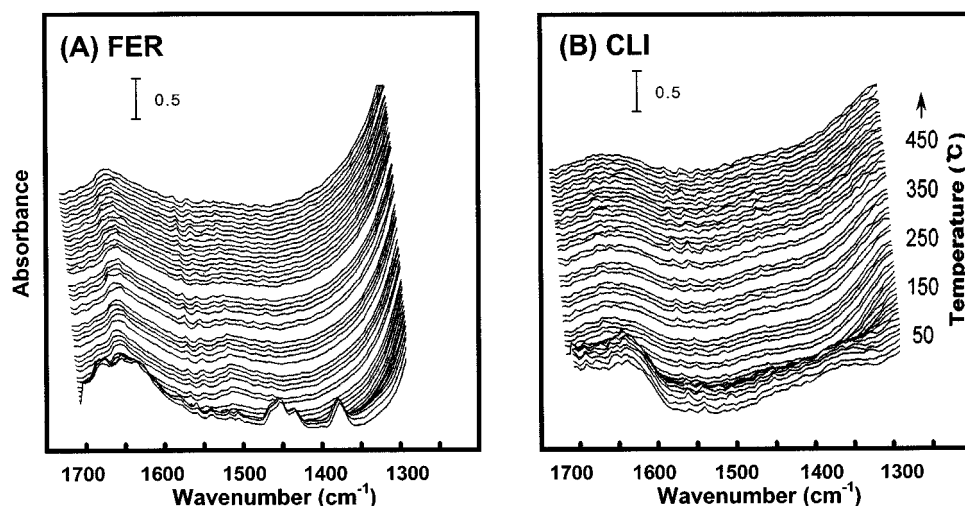
Figure 5. 3D IR spectra of adsorbed 1-butene FER (A) and CLI (B) zeolites. Zeolite was exposed to 1-butene at 30 °C and evacuated with temperature increasing to 550 °C with a ramp of 16 °C min^{-1}.
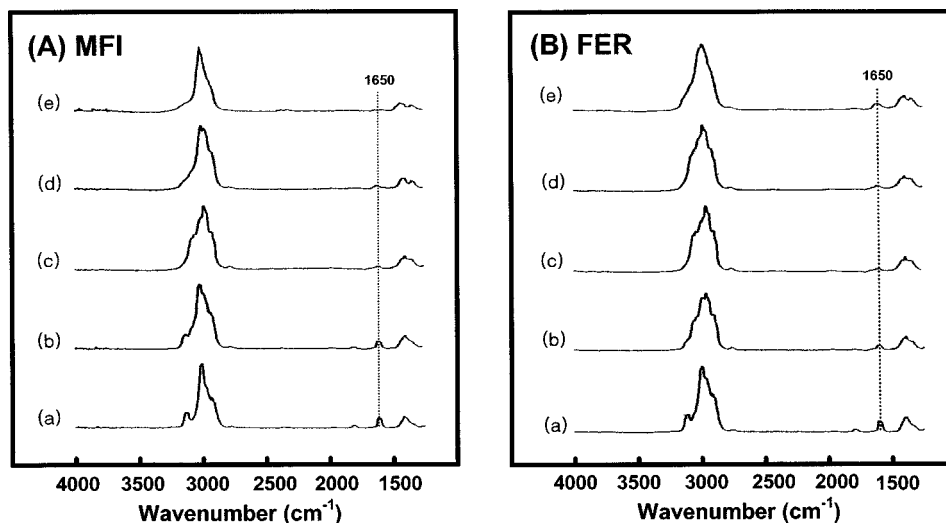

Figure 6. IR spectra of gas phase in the 1-butene conversion over MFI (A) and FER (B) zeolites. Initial pressure of 1-butene was 1.0 kPa and IR spectra were recorded at 30 (a), 200 (b), 250 (c), 350 (d) and 450 °C (e).

The skeletal isomerization of 1-butene in the *in situ* IR cell on a zeolite catalyst was investigated. Gas composition was monitored from IR spectra of the gas phase, while the adsorbed species on the zeolite were deduced from IR spectra recorded from transmitted light through the zeolite wafer. Figure 6 shows the IR spectra of the gas phase contacting the MFI and FER zeolites. The IR spectrum recorded at 30 °C was the same with that of 1-butene. The IR spectra, however, recorded at elevated temperatures were different according to zeolite species. The band of 1650 cm^{-1} assigned to a C=C double bond was weakened on the MFI zeolite above 200 °C and disappeared at 400 °C (figure 6(A)). Butene converts to paraffin on the MFI zeolite through cracking of oligomers into various hydrocarbons. In contrast, the band at 1650 cm^{-1} was retained on the FER zeolite even at 450 °C, indicating a negligible consumption of olefin. The skeletal isomerization between butene iso-

mers is predominant on the FER zeolite, and thus, the total amount of olefin is sustained. These results confirm the high selectivity for skeletal isomerization of the FER zeolite and the low selectivity of the MFI zeolite, similar to the reaction results in table 1.

IR spectra of adsorbed butene species, as well as of the gas phase were different according to zeolite species. As shown in figure 7, the sequential 3D spectra of butene species adsorbed on the MFI zeolite recorded under 1 kPa of 1-butene were almost the same as those recorded under evacuation (figure 3(A)). The formation of polymeric species was also confirmed by the band of 1505 cm^{-1}. In contrast, the sequential 3D spectra obtained from the FER zeolite under 1 kPa of 1-butene were different from those recorded under evacuation (figure 5(A)). A small amount of polymeric species formed at elevated temperatures. At higher temperatures all of the absorption bands relating to
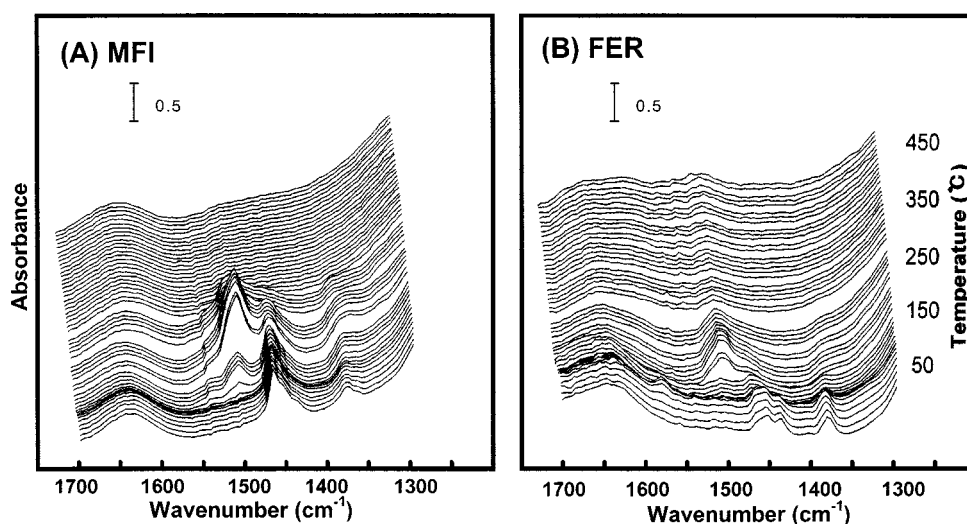
Figure 7. 3D IR spectra of adsorbed 1-butene in the 1-butene conversion over MFI (A) and FER (B) zeolites. Initial pressure of 1-butene was 1.0 kPa and temperature increasing to 450 °C with a ramp of 16 °C min^{-1}.

hydrocarbon disappeared on the MFI zeolite, while a trace of 1505 cm^{-1} was retained on the FER zeolite, even at 450 °C.

The fact that the same 3D IR spectra are obtained from the MFI zeolite regardless of evacuation and under 1 kPa of butene, indicates filling of the pore with adsorbed butene species, even under evacuation conditions. Oligomers with high boiling points are already formed with just exposure of the MFI zeolite to 1-butene at room temperature, and thus, adsorbed butene species can be retained under evacuation. On the FER zeolite, most of the adsorbed butene molecules do not form oligomers, and can be easily desorbed with evacuation. However, some of 1-butene molecules are distributed in the pore of the FER zeolite under 1 kPa of 1-butene. Most of the butene molecules located sparsely at the intersections of channels isomerize to isobutene through monomolecular skeletal isomerization, but a small part with large kinetic energy react with each other and form oligomers. The oligomer converts to polymeric species at elevated temperatures, showing the band of 1505 cm^{-1}. Retention of the band on the FER zeolite at 450 °C, even though the intensity is very low, indicates the difficulty of desorption due to high restriction to transfer along the pore. It is well known that the selectivity for the skeletal isomerization of the FER zeolite enhances with carbon deposit [17]. A small amount of carbon deposit increases the potential behavior, suppressing bimolecular reaction.

The selectivities of FER and CLI zeolites for the skeletal isomerization of n-butene are exceptional, while those of MFI and BEA zeolites are considerably low at a high conversion level. IR spectra recorded under the reaction conditions suggest that the molecularity of the predominant reaction on zeolite catalyst is dependent on its pore structure and the difference in the molecularity induces the difference in the selectivity. Restriction of oligomer formation due to the pore structure on FER and CLI zeo-

lites enhances the preference to the monomolecular reaction.

Both FER and CLI zeolites contain a two-dimensional channel system consisting of 10-rings intersected by 8-rings [18], so the cross sectional area of the pore must be reduced periodically. The potential energy of an adsorbed butene molecule is at its minimum at the channel intersection, and thus, butene molecules are sparsely distributed in the pore of CLI and FER zeolites. The sparse distribution suppresses bimolecular oligomerization, enhancing the monomolecular skeletal isomerization.

The pore of the MFI zeolite is composed of 10-rings and that of the BEA zeolite of 12-rings [19]. The potential barrier of MFI and BEA zeolites for transfer of the butene molecule along the pore is negligible compared to that of FER and CLI zeolites. The easy transfer of activated butene molecules brings about colliding with each other and forming oligomers. Various hydrocarbons are produced from oligomers, showing low selectivity for isobutene.

IR spectra recorded with heating may be more plausible evidence for the formation of oligomers on the MFI and BEA zeolites, and for the monomolecular behavior on the FER and CLI zeolites, if the chemical state of oligomers formed in MFI and BEA zeolites can be assigned. However, the considerable difference in the IR spectra of adsorbed butene according to zeolite species strongly suggests the difference in the reaction molecularity between the skeletal isomerization and oligomerization of butene.

4. Conclusions

The IR spectra of butene adsorbed on zeolite recorded with heating, are different according to its pore structure. Butene adsorbed on MFI and BEA zeolites, showing poor selectivity for isobutene, forms oligomers and converts to polymeric species at elevated temperatures. On the other hand, the formation of oligomers is suppressed on FER and

CLI zeolites, which shows an exceptional selectivity for skeletal isomerization. The specific pore structures of FER and CLI zeolites suppressing the bimolecular reaction, are ascribed to their high selectivity for monomolecular skeletal isomerization.

Acknowledgement

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