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The reversible skeletal isomerization between *n*-butenes and iso-butene over solid acid catalysts

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Abstract

The reversibility of skeletal isomerization between *n*-butenes and iso-butene has been studied over various solid acid catalysts including ferrierite and ZSM-5 zeolites, mesoporous materials and amorphous alumina in order to identify the cause for their different selectivities for skeletal isomerization. A remarkable selectivity for the reverse skeletal isomerization of iso-butene to *n*-butenes is found from ferrierite, fluorinated alumina with low fluorine loading and the KIT-1 mesoporous material with low aluminium content; which also demonstrate high selectivity for forward skeletal isomerization. Catalysts that are not selective for forward isomerization exhibit poor selectivity for reverse isomerization. The preference for multimolecular oligomerization due to high concentrations of activated reactants in the pores of nonselective catalysts reduces their selectivity for skeletal isomerization. Thus, the suppression of oligomerization over the selective catalyst makes the cracking of oligomers impossible and increases selectivity. This is achieved by a sparse distribution of activated reactants caused by specific pore structures or low concentrations of strong acid sites. The reversibility of skeletal isomerization and the adsorbed state of butenes are discussed in relation to the monomolecular reaction path.

Keywords: iso-Butene skeletal isomerization; Reversibility of skeletal isomerization; Acid site concentration; Monomolecular reaction

1. Introduction

Skeletal isomerization of *n*-butenes over solid acid catalysts is an attractive route for producing iso-butene, the raw material of methyl *tert*-butyl ether (MTBE), from C_4 raffinate. Moreover, the fact that selectivity for iso-butene in the conversion of *n*-butenes varies remarkably among catalysts is an interesting phenomenon in itself [1,2]. Ferrierite (FER) zeolite shows exceptionally high selectivity, while ZSM-5 (MFI) zeolite shows poor selectivity [3]. In another example, the selectivity for iso-butene of a fluorine-modified alumina catalyst changes with the loading level of fluorine [4]. Selectivity of the catalyst with low fluorine loading is high, while with high fluorine it is poor.

The high selectivity of FER zeolite for iso-butene has been attributed to its specific pore structure and mild acidity [5]. However, the contribution of pore structure to the high selectivity is not a sufficient explanation, because amorphous F/Al_2O_3 [6–8] and W_2O_5/Al_2O_3 [9] catalysts also show a high selectivity. In addition, the type and strength of acid sites influ-

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ence selectivity, but they are not sufficient factors to explain the difference in the selectivities between FER and MFI zeolites [3]. Very recently, Seo et al. [10] suggested that the selectivity for skeletal isomerization can be determined by the distribution of adsorbed butene molecules on the catalyst surface. If the skeletal isomerization is assumed to proceed via monomolecular reaction, the suppression of bimolecular reaction producing various hydrocarbons can be considered the common characteristic of selective catalysts. Low possibility for oligomerization due to the specific pore structure of FER zeolite and the low concentration of strong acid sites on the fluorinated alumina catalyst with low fluorine loading comparatively accelerate the monomolecular reaction path resulting in high selectivity to iso-butene. This view on the cause of the high selectivity is adoptable to zeolite as well as amorphous catalysts regardless of their pore structures, but it remains to be verified whether skeletal isomerization in fact proceeds by monomolecular reaction.

The observation of intermediates is the most reliable evidence for the reaction molecularity. Protonated cyclopropane rings [11] or carbenium ions [8] have been suggested as intermediates for iso-butene formation in the monomolecular reaction path, but no intermediate has been confirmed experimentally. Although a kinetic analysis may be helpful to deduce reaction molecularity, the possibility of many reactions occurring simultaneously may reduce the feasibility of this approach.

Participation of two or more *n*-butene molecules should be required for oligomerization, but only one *n*-butene molecule is involved in the monomolecular reaction. Various products may be formed by cracking dimers and oligomers, hereafter called as "oligomer". Accordingly a high reversibility of skeletal isomerization between iso-butene and *n*-butenes is not expected through oligomer formation, as mentioned by Cheng and Ponec [7]. Therefore, the reversibility of skeletal isomerization may contribute more evidence for the monomolecular reaction path of 1-butene to iso-butene.

In this paper, reversibility of skeletal isomerization between *n*-butenes and iso-butene is investigated over various catalysts showing remarkable differences in forward isomerization. FER and MFI zeolites, KIT-1 mesoporous materials and amorphous alumina catalysts with different fluorine loadings were used. The adsorption–desorption behavior of iso-butene was also studied by FT-IR spectroscopy to observe differences in the adsorbed state of iso-butene on the selective and nonselective catalysts.

2. Experimental

The detailed information on the catalysts used in this study such as fluorinated alumina [4], FER and MFI zeolites [3] and KIT-1 mesoporous materials [12] is described elsewhere. Numbers in the parentheses of $F(x)/Al_2O_3$ catalysts indicate wt% of fluorine loading. The number in the KIT-1(y) catalyst parentheses indicates the Si/Al molar ratio of the mesoporous material.

The apparatus and procedure for skeletal isomerization reaction of iso-butene are similar to those for the skeletal isomerization of 1-butene reported in our previous work [3]. The isomerization reaction of iso-butene or 1-butene was carried out under 31 kPa of iso-butene or 1-butene at 450°C. 2-Butenes were not evaluated as products of the skeletal isomerization of 1-butene, while *n*-butenes (1-butene and 2-butene) were considered as products of the reverse isomerization of iso-butene. The conversion of 1-butene or iso-butene is defined as the mole percentage of reactant consumed. In addition, the selectivity to iso-butene or *n*-butenes is defined as the mole percentage fraction of skeletally isomerized products to the consumed reactant.

The acidity of the catalysts was determined by the temperature-programmed desorption (TPD) of ammonia [4]. The adsorbed amount of iso-butene or 1-butene on the catalyst was measured by a gravimetric apparatus equipped with a quartz spring [4].

The adsorption–desorption behavior of iso-butene on the catalyst was monitored by an ATI Mattson, Genesis Series FT-IR spectrometer equipped with an in situ quartz cell at a resolution of $4\ \text{cm}^{-1}$. A self-supporting wafer of 10 mg was placed in the in situ IR cell, and then evacuated under a vacuum of 2.5×10^{-5} kPa at 550°C for 2 h. iso-Butene was adsorbed at 25°C, 300°C or 450°C for 0.5 h under 0.75 and 6.8 kPa of the pressure of iso-butene. Finally, the catalyst was evacuated for 0.5 h before the IR spectra was recorded.

Simulations of the favorable location of iso-butene molecules adsorbed in FER and MFI zeolites were carried out using the Cerius^2 Sorption Module equipped with a Monte Carlo statistical mechanics software corresponding to fixed pressure, adopting the Burchart-Universal force field, as described elsewhere [10].

3. Results and discussion

n-Butenes (1-butene and 2-butene) are converted on acid catalysts to iso-butene through skeletal isomerization, and to C_2, C_3 and C_5^+ hydrocarbons through oligomerization followed by cracking. If iso-butene is the major product, the conversion of *n*-butenes is limited by an equilibrium among butenes, namely to 38.5% at 450°C [8]. Therefore, *n*-butene conversion increases with increasing cracked products, while selectivity to iso-butene decreases. Therefore, selectivity to iso-butene is considerably dependent on the extent of oligomerization followed by cracking. FER zeolite, in which 1-butene molecules distribute separately in the pores because of the specific pore structure of their material, shows a high selectivity for iso-butene due to the suppression of oligomerization [3]. On fluorinated alumina catalysts with low fluorine loading [4], and KIT-1 mesoporous material with low aluminum content [12], low concentrations of strong acid sites induce sparse adsorption of the activated butene molecules which suppress oligomerization, resulting in high selectivity.

The conversions and selectivities for reversible skeletal isomerizations between 1-butene and iso-butene over various catalysts are summarized in Table 1. These data reveal that the selective catalysts for forward isomerization of 1-butene to iso-butene such as the FER zeolite, F(0.008)/Al_2O_3 and KIT-1(97) catalysts show high selectivity for the reverse isomerization of iso-butene to *n*-butenes. On the other hand, the nonselective catalysts in forward isomerization such as MFI zeolite, F(0.040)/Al_2O_3 and KIT-1(14) catalysts exhibit low selectivity to *n*-butenes in the reverse isomerization of iso-butene. Therefore, it is clear that the reversibility of skeletal isomerization between *n*-butenes and iso-butene is high on the catalysts selective in the forward isomerization, while the opposite is observed for the nonselective catalysts. This suggests that skeletal isomerization and oligomerization followed by cracking proceed independently. The preference for one of these reactions is determined by catalytic characteristics, resulting in the selectivity for skeletal isomerization.

Table 1 also shows that the conversion levels and the product distributions of the nonselective catalysts are different. The conversion is high on MFI zeolite, while those of F(0.040)/Al_2O_3 and KIT-1(14) catalysts are low. In addition, as shown in Table 2, propene and pentenes are the major products on F(0.040)/Al_2O_3 and KIT-1(14) catalysts, while various hydrocarbons are formed on the MFI zeolite. Fast diffusion and low cracking activity on F(0.040)/Al_2O_3 and KIT-1(14) catalysts due to their large pore size and mild acidity prevent further reactions of primary cracked products

Table 1
Conversions and selectivities of the forward and reverse skeletal isomerizations between 1-butene and iso-butene over various solid acid catalysts[a]

Catalyst	1-Butene→iso-butene		iso-Butene→*n*-butenes	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
FER	11.8	96.1	20.2	95.0
MFI	84.3	11.0	83.1	11.8
Al_2O_3	—	—	1.2	>99.0
F(0.008)/Al_2O_3	9.5	96.9	12.6	95.6
F(0.040)/Al_2O_3	38.5	60.6	39.3	57.8
KIT-1(14)	12.6	71.1	12.2	61.7
KIT-1(40)	7.8	81.5	11.0	65.0
KIT-1(54)	1.5	>99.0	6.8	73.8
KIT-1(97)	—	—	4.7	78.5

[a] Reaction temperature, 450°C; WHSV, 13.0 h^{-1}; $P_{1\text{-butene}}$, 31 kPa; $P_{\text{iso-butene}}$, 31 kPa.

Table 2
Product distributions of forward and reverse skeletal isomerizations over nonselective catalysts[a]

	Reaction					
	1-Butene→iso-butene			iso-Butene→n-butene		
	MFI	F(0.040)/Al_2O_3	KIT-1(14)	MFI	F(0.040)/Al_2O_3	KIT(14)
Conversion (%)	84.3	38.5	12.6	83.1	39.3	12.2
Composition of product (%)						
C_2	9.8	0	0	10.5	0	0
$C_2^=$	16.6	0	0	20.1	0	0
C_3	31.6	22.9	13.6	31.0	22.8	22.8
$C_3^=$	14.5	1.4	0	17.2	3.7	6.0
n-C_4	8.5	0	0	7.1	0	0
n-$C_4^=$	—	—	—	11.8	57.8	61.7
iso-$C_4^=$	11.0	60.6	71.1	—	—	—
$C_5^{+,b}$	8.0	15.1	15.4	2.4	15.7	9.5

[a] Reaction temperature, 450°C; WHSV, 13.0 h^{-1}; $P_{1\text{-butene}}$, 31 kPa; $P_{\text{iso-butene}}$, 31 kPa.
[b] C_6 and higher hydrocarbons.

of the oligomer, resulting in a simple product distribution and low conversion. The more interesting finding is the similarity in the by-product compositions of forward and reverse isomerizations. This finding indicates that oligomerization followed by cracking, which constitutes the side reaction in skeletal isomerization, proceeds through a similar oligomeric intermediate in both reactions.

In consecutive reactions, the selectivity to the first product varies with conversion level. A high selectivity for the first product is usually observed at low conversion. The relationship between selectivity for n-butenes and conversion of iso-butene in the reverse isomerization shows that skeletal isomerization is not a consecutive reaction. As shown in Fig. 1, the relationship is different over F(0.008)/Al_2O_3 and F(0.040)/Al_2O_3 catalysts. The conversion increases steadily with the increase of the loading amount of F(0.008)/Al_2O_3 catalyst, but the decrease of selectivity is not considerable. This observation is quite different from the result for the F(0.040)/Al_2O_3 catalyst which is nonselective in skeletal isomerization. Therefore, it is most likely that high selectivity for skeletal isomerization is due to the characteristics of catalyst itself, rather than to the low conversions.

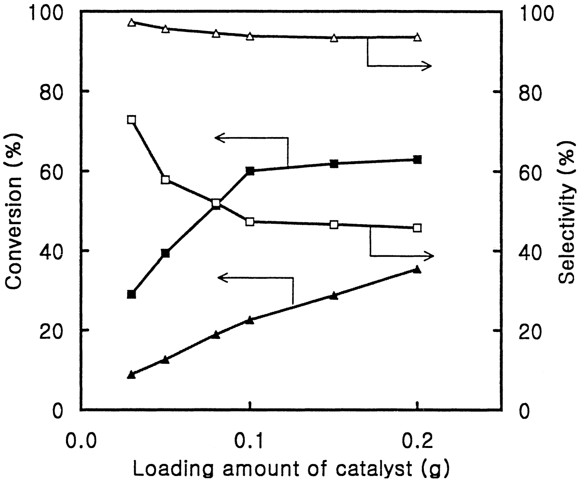


Fig. 1. Skeletal isomerization of iso-butene to n-butenes over fluorinated alumina catalysts with various amounts of catalyst loadings at 450°C, $P_{\text{iso-butene}}$=31 kPa. F(0.008)/Al_2O_3 (△), and F(0.040)/Al_2O_3 (□)

The difference in the selectivity for skeletal isomerization over solid acid catalysts may be deduced from the adsorption–desorption properties of 1-butene and iso-butene, because the reaction molecularity is strongly dependent on the surface concentrations of activated reactant. The probability of monomolecular reaction prevails at low concentrations of activated reactant on the catalyst surface, while high concentrations of activated reactant accelerates reactions which involve several reactant molecules. Actually an enhancement of the selectivity for skeletal isomeriza-

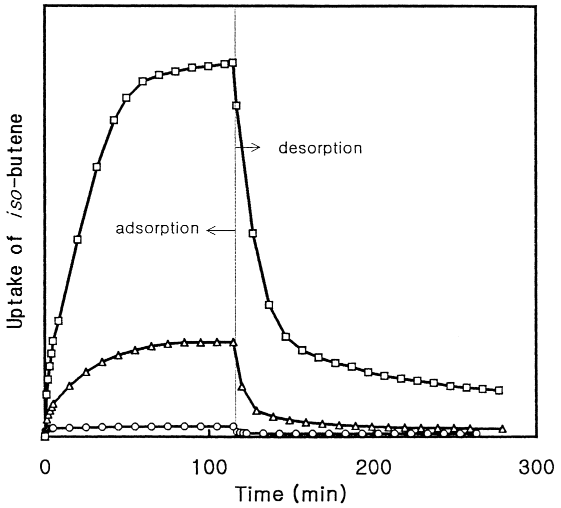


Fig. 2. Adsorption–desorption behaviors of iso-butene over Al_2O_3 (○), F(0.008)/Al_2O_3 (△), and F(0.040)/Al_2O_3 (□) catalysts at 25°C. Adsorption is made by exposing the catalyst to 31 kPa of iso-butene at adsorption process.

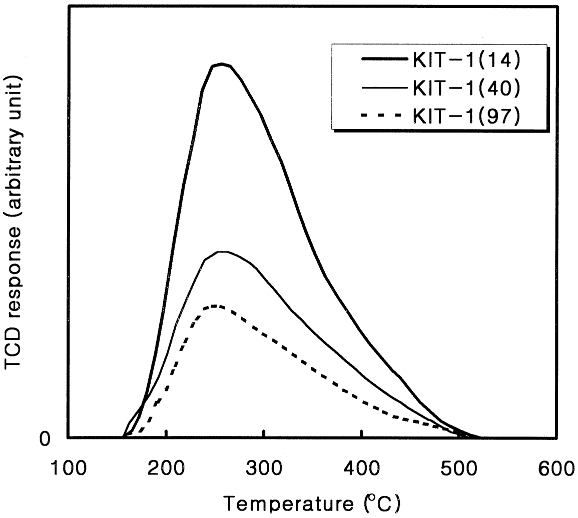


Fig. 3. Ammonia TPD profiles for KIT-1 catalysts with various Si/Al ratios.

tion has been reported when reducing the partial pressure of 1-butene over FER and MFI zeolites regardless of their levels of selectivity [3].

Fig. 2 shows the adsorption–desorption behavior of iso-butene over fluorinated catalysts. iso-Butene is scarcely adsorbed over the Al_2O_3 catalyst at 25°C. The F(0.008)/Al_2O_3 catalyst with low fluorine loading adsorbs a little iso-butene, which can be desorbed completely by evacuation. On the other hand, a large amount of iso-butene is adsorbed on the F(0.040)/Al_2O_3 catalyst with high fluorine loading, and some iso-butene is retained after evacuation. The variation of the adsorbed amount and reversibility of iso-butene with the loading level of fluorine reflect the differences in the adsorbed states of iso-butene on F(0.008)/Al_2O_3 and F(0.040)/Al_2O_3 catalysts. These findings are similar to the adsorption–desorption behaviors of 1-butene over the same catalysts [4].

The slow desorption of iso-butene can be attributed to either a strong adsorption of butene on F(0.040)/Al_2O_3 catalyst or to the formation of high boiling-point materials formed from adsorbed butene molecules. The slow desorption of iso-butene was also observed from the KIT-1(14) catalyst with a low Si/Al molar ratio. Fig. 3 shows TPD profiles of ammonia from KIT-1 mesoporous materials with various Si/Al molar ratios. It is clear that the number of acid sites increases with increased aluminum content in the mesoporous material framework. This finding confirms that high concentrations of acid sites on the KIT-1(14) catalyst lead to slow desorption.

In addition to the strong adsorption, the interaction among adsorbed iso-butene molecules also contribute to slow desorption. The activated iso-butene molecules on strong acid sites interact with each other to form high-boiling aggregates, which desorb slowly during the evacuation process. There are some differences for KIT-1(14) and KIT-1(97) catalysts in the absorption band at 1550–1650 cm^{-1} relating to double bonding [13] as shown in Fig. 4. These spectra were recorded as a difference mode with a background of evacuated KIT-1 catalysts, recording the net absorbance due to adsorbed iso-butene. The adsorbed amount of iso-butene is small at low pressure (lower spectra) and large at high pressure (upper spectra). The band shapes of adsorbed iso-butene on the KIT-1(97) catalyst (Fig. 4) are identical at 25°C and 300°C, while the adsorbed amount decreases with the adsorption temperature. On the other hand, a shoulder at 1580 cm^{-1} is observed at 450°C. Since the skeletal isomerizations were carried out at 450°C, the shoulder band might be the contribution of the reaction products. The shoulder at 1580 cm^{-1} is more significant on the KIT-1(14) catalyst (Fig. 4). The shoulder does

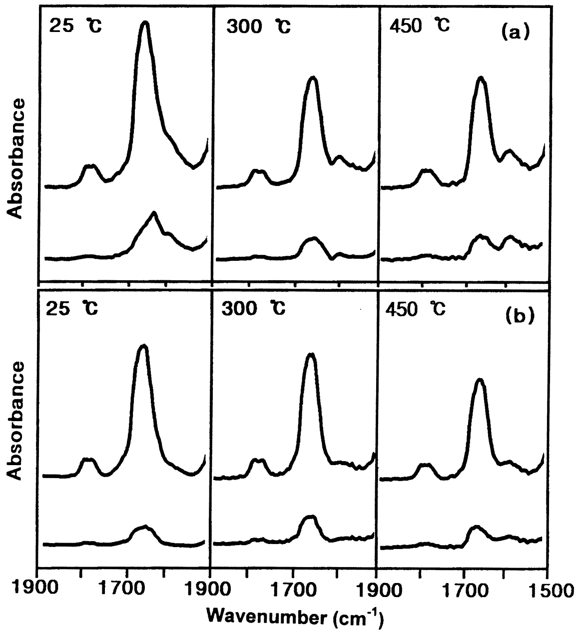


Fig. 4. Difference IR spectra of adsorbed iso-butene on (a) KIT-1(14), and (b) KIT-1(97) at various temperatures. $P_{\text{iso-butene}}$= 0.75 kPa (lower) and $P_{\text{iso-butene}}$=6.8 kPa (upper).

not clear when the catalyst is exposed to low pressure iso-butene at 25°C, but can be observed with a remarkable intensity by exposing the sample to high pressure iso-butene at 300°C and 450°C. Although no assignment of the band at 1580 cm^{-1} has been made yet, it is certain that the shoulder must be related to a double bond. Therefore, the new shoulder indicates the change in double bond of adsorbed iso-butene on the nonselective catalyst with high concentrations of strong acid sites. The fact that the intensity of the band at 1580 cm^{-1} is very weak on the KIT-1(97) catalyst with low concentrations of strong acid sites points to a difference in the adsorbed states or distribution of adsorbed iso-butene, due to variation of the type of interaction between the catalyst surface and adsorbed iso-butene when the concentrations of strong acid sites change.

Although there are several uncertainties in molecular dynamic calculations, a computer simulation of distribution in the reactant zeolite framework provides some helpful insights on reaction molecularity. Fig. 5 shows the simulated distribution of iso-butene on zeolite under 1 bar and at 25°C. iso-Butene molecules prefer to distribute at the intersection of channels of the FER zeolite with few possibilities to contact each other (Fig. 5(a)). On the other hand, iso-butene molecules are distributed closely to each other in the channel of MFI zeolite (Fig. 5(b)). We already reported a similar behavior of 1-butene on FER and MFI zeolites, and the difference in the distribution of 1-butene molecules was suggested to be the determining factor for the selectivity for skeletal isomerization [10]. The sparse adsorption of butene molecules in FER zeolite suppressed oligomerization, resulting in high selectivity for monomolecular skeletal isomerization. Correspondingly, the close adsorption of iso-butene in MFI zeolite is a probable reason for its low

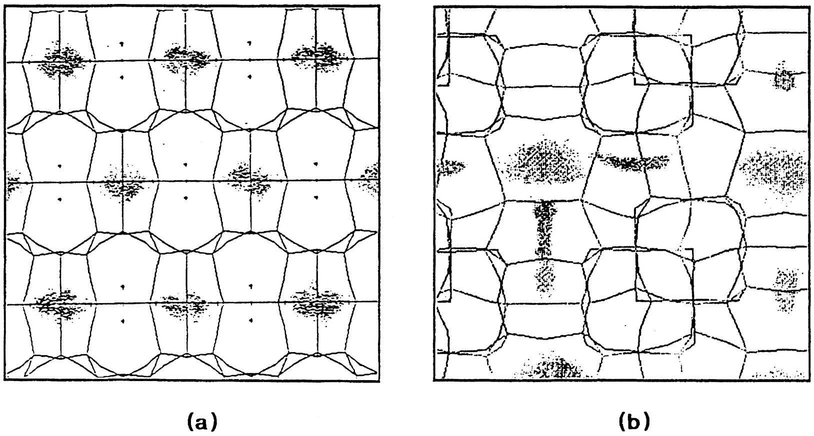
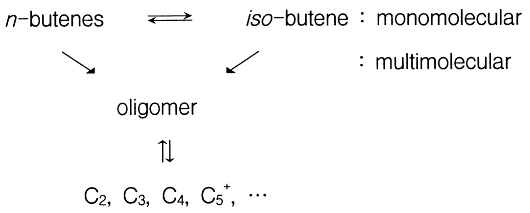


Fig. 5. Simulated distributions of iso-butene adsorbed on (a) FER, and (b) MFI zeolites at 27°C and 1 kPa; accumulation: 10^6 iterations.

selectivity for skeletal isomerization due to a high preference for oligomer formation.

The highly selective catalysts for skeletal isomerization not only show high reversibility in forward and reverse isomerization; they also exhibit common characteristic in the sparse distribution of butene molecules. Due to the restrictions of specific pore structure or low concentrations of acid sites, butene molecules are distributed distantly in selective catalysts. The similar conversion levels and product distribution observed from forward and reverse isomerization on nonselective catalysts indicate that side products are cracked from oligomers formed from *n*-butenes or iso-butenes. These findings suggest that skeletal isomerization and oligomerization followed by cracking are competitive on acid catalysts with different reaction molecularities, as shown below:



Since there are various cracking reaction paths from oligomers, the probability of reversibility between butenes and oligomer must be low [14]. Therefore, selectivity for skeletal isomerization depends strongly on the extent of oligomer formation. High concentrations of activated reactant accelerates multimolecular oligomerization and thus reduces selectivity. On the other hand, sparse distribution of the activated reactant induces the monomolecular reaction. High reversibility between *n*-butenes and iso-butene on the selective catalysts also supports the monomolecular character of skeletal isomerization. As a common characteristic of the selective catalysts, we suggest the activation of sufficient butene molecules to permit skeletal isomerization, but the suppression of multimolecular oligomerization due to sparse distributions of reactant on the catalyst surface.

4. Conclusions

The selectivities for reverse skeletal isomerization from iso-butene to *n*-butenes are high on FER, modified alumina with low fluorine loading and KIT-1 mesoporous material with a low aluminum content. Since the selectivities for forward isomerization are also high on these catalysts, good reversibiliy is observed on the selective catalysts. Similar conversion levels and product composition for forward and reverse isomerization are observed on nonselective catalysts, suggesting that oligomerization followed by cracking proceeds along different reaction paths than skeletal isomerization. Desorption behavior and IR spectra of adsorbed butene on the selective catalyst indicates monomeric adsorption. Activated butene on acid site, either *n*-butene or iso-butene, isomerizes skeletally through a monomolecular reaction, when oligomerization is suppressed as a consequence of sparse distribution. Sparse distribution of activated butene molecules favors the monomolecular reaction and reduces multimolecular oligomerization, resulting in high selectivity for skeletal isomerization.

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