Influence of the fluorine loading level on the skeletal isomerization of 1-butene over fluorine-modified alumina

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γ-alumina catalysts modified with different weight loadings of fluorine have been used for skeletal isomerization of 1-butene in order to investigate the effects of the fluorine loading level on the conversion of 1-butene and the selectivity to isobutene formation. Increasing the actual loading of fluorine up to 0.012 wt% led to an increase in conversion of 1-butene over fluorine-modified γ-alumina catalysts, while the high selectivity to isobutene remains almost unchanged. On the other hand, a clear trend of increasing 1-butene conversion with a decreasing selectivity to isobutene is observed for the γ-alumina catalysts with higher loadings of fluorine. An analysis of the results from the thermal analysis, NH_3 temperature-programmed desorption, infrared and the 1-butene sorption measurments clearly indicates that the number of strong acid sites in the modified γ-alumina catalysts is greatly enhanced at fluorine loadings higher than 0.012 wt%, leading to the acceleration of 1-butene oligomerization followed by cracking to light hydrocarbons. Therefore, the 1-butene isomerization selectivity from fluorine-modified γ-alumina catalysts can be understood in terms of a competition between the monomolecular and bimolecular reaction pathways, which highly depend on the concentration of strong acid sites.

Keywords: 1-butene, skeletal isomerization, fluorine-modified alumina, acid site concentration, monomolecular reaction

1. Introduction

The demand for methyl tertiary-butyl ether (MTBE) and ethyl tertiary-butyl ether (ETBE) as octane rating promoter increases by regulating the amounts of aromatic compounds in gasoline, in order to reduce cancer-inducing materials in the exhaust gas of engines. The demand for isobutene, a raw material of oxygenated ethers, is also increased, and there is a growing interest in the process of producing isobutene from C_4 raffinates of cracking process [1–3].

n-butene can be converted into various hydrocarbons over solid acid catalysts. These products include various hydrocarbons such as C_2, C_3 and C_{5+} as well as isobutene. C_2, C_3 and C_{5+} hydrocarbons are formed through dimerization or oligomerization followed by cracking and isobutene is formed through skeletal isomerization. A geometric isomerization between *cis*-2-butene and *trans*-2-butene and a double-bond migration can proceed on solid acid catalysts simultaneously. Therefore, the product distribution is very complicated because the extent of reaction varies according to reaction conditions and catalysts.

Although many by-products can be formed from 1-butene, several catalysts such as ferrierite (FER) [4], MCM-22 [5], aluminophosphate [6,7], F/Al_2O_3 [8–10] and WO_3/Al_2O_3 [11] are reported to show exceptional selectivity for the skeletal isomerization producing isobutene. This phenomenon is considerably peculiar to the fact that the selectivity to isobutene is very low over catalysts such as MFI zeolite [12] and silica–alumina [3]. Mooiweer et al. [4] reported that the high selectivity was attributed to the product shape selectivity and to the mild acidity of FER zeolite. On the other hand, Guisnet et al. [13] suggested that coke deposit with aryl carbeniums in the pore works as an active site. It is not adequate to explain the difference in the selectivity of zeolite catalysts with the pore structure, because the selectivity is also high over fluorine-modified alumina catalysts with no regular pore structures [10]. It is also not adequate to explain the high selectivity of amorphous catalysts according to acidity, because there are no significant differences in the acidity of MFI and FER zeolites whose selectivities to isobutene are considerably different [14]. Seo et al. [12] explained that the high selectivity to isobutene is due to the distant distribution of the activated butene molecules in the confined pore structure of FER zeolite. The low possibility of dimerization in FER zeolite pore due to distant location suppresses the dimerization followed by cracking, enhancing the selectivity to skeletal isomerization. A further increase of selectivity enhancing the isolation effects of 1-butene by carbon deposition in the pores was also reported [15].

Monomolecular [7,11,12,14–16] and bimolecular [4,17] reaction paths are considered to be possible ways for the conversion of 1-butene to isobutene. 1-butene molecules activated on acid sites can be solely isomerized through protonated cyclopropane rings [18] or carbenium ions [8] by monomolecular reaction. In bimolecular reactions, dimerized butenes isomerize to suitable octene isomers and are cracked to isobutene. Although there is no positive evidence for the monomolecular skeletal isomerization, reports about the low selectivity to isobutene in the cracking of

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some octene isomers [19] and the change in the IR band of butene on nonselective catalysts [16,20] reduce the possibility of isobutene formation by bimolecular reactions [19].

Cheng et al. [10] suggest that the selectivity to isobutene in the skeletal isomerization varies according to type of acid site. On fluorine-modified alumina catalysts, the reaction proceeds on Brønsted acid sites through a bimolecular path, but the monomolecular reaction proceeds on the Lewis acid sites. The increase in the selectivity of fluorine modification was explained by the increase of the number of Lewis acid sites under the assumption of monomolecular skeletal isomerization. Judging from what has been investigated thus far, it would be unreasonable to infer that the acidity or the pore structure alone could be taken as the essential cause of the high selectivity consistently applied in various catalysts, although the acidity, pore structure, and the type of acid sites were important for determining the selectivity.

If the distribution of activated 1-butene molecules on the catalyst surface were a primary factor determining the selectivity to isobutene, the high selectivities of amorphous and zeolite catalysts could be explained by the same reason. This study aims to investigate the skeletal isomerization of 1-butene on alumina catalysts modified with fluorine of 0.005–0.04 wt%. We have analyzed the factors determining the selectivity to isobutene by the relationship between the conversion of 1-butene and the selectivity to isobutene over various catalysts with different loading levels of fluorine, the acidic properties of fluorine-modified alumina, and the adsorption–desorption behavior of 1-butene according to the loading level of fluorine. We have also investigated the variation of the selectivity with the loading level of fluorine from the deposited amount of carbon during the reaction and the desorption behavior of adsorbed 1-butene with IR measurement.

2. Experimental

2.1. Catalyst preparation

γ-alumina (JRC-ALO-2) with a BET surface area of 235 $m^2\,g^{-1}$ was provided by the Catalysis Society of Japan. The loading of fluorine was carried out by the impregnation of alumina with an aqueous ammonium fluoride (Aldrich, >99%) solution followed by drying at 373 K. The loading levels of fluorine varied from 0.25 to 3 wt% alumina on the basis of fluorine. Finally, the fluorine-loaded samples were calcined in air at 823 K for 3 h.

The remaining amount of fluorine after calcination was analyzed by wet methods using an ORION ion meter, model 720A. First, 0.2 g of the sample was dissolved in an NaOH solution in a Ni crucible, followed by neutralizing with HCl solution. Then the amounts of fluorine were determined by using the electrode for F^- after mixing 50 ml of the sample and 50 ml of trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid monohydrate. The loading of fluorine on alumina catalysts before and after the calcination are summarized in table 1.

Larger amounts of fluorine lead to larger amounts of fluorine remaining on alumina. However, the remaining amount of fluorine after calcination was found to be less than one-hundredth of the amount initially added. As the added amount of fluorine before the calcination is meaningless, the loading amounts are written in parentheses as, for example, F(0.005)/Al_2O_3.

2.2. Catalyst characterization

The acidity of the catalyst was investigated by temperature-programmed desorption (TPD) of ammonia. About 0.2 g of the sample was activated in a He stream at 823 K for 2 h, then ammonia was introduced over the sample at 423 K with a pulse. The sample was purged in a He stream at the same temperature for 2 h in order to eliminate physisorbed ammonia. The NH_3-TPD profiles were obtained in a He stream of 200 $ml\,min^{-1}$ by increasing from 423 to 873 K with a ramping rate of 10 $K\,min^{-1}$. The amount of ammonia desorbed from the sample was determined with a thermal conductivity detector (TCD).

The N_2 adsorption on samples was measured on a home-built volumetric apparatus at 77 K. BET surface areas of Al_2O_3 and F(0.04)/Al_2O_3 catalysts calculated from adsorption isotherms of N_2 are 235 and 212 $m^2\,g^{-1}$, respectively. These values are approximately the same, indicating that the change in the pore structure of alumina is not significant with the loading of fluorine.

The adsorbed amount of 1-butene was measured by a gravimetric apparatus equipped with a quartz spring [21]. The catalyst of 0.2 g was evacuated at 673 K for 1 h, and then exposed to 30.4 kPa of 1-butene at 300 K. The weight change of the catalyst was recorded during the adsorption–desorption process of 1-butene.

The adsorption–desorption behavior of 1-butene on fluorine-modified catalysts was examined with an ATI Mattson, Genesis series Fourier transform infrared spectrometer with an *in situ* quartz cell at a resolution of 4 cm^{-1}. A self-supporting wafer of 10 mg catalyst was placed in the cell, and evacuated under a vaccum of 2×10^{-4} Torr, 823 K for 1 h. 1-butene was adsorbed on the catalysts at 723 K

Table 1
Loading of fluorine on alumina catalysts before and after calcination.

Catalyst	F(I)	F(II)	F(III)	F(IV)	F(V)	F(VI)
Before calcination (wt%)	0.25	0.5	0.75	1.0	2.0	3.0
After calcination (wt%)	0.005	0.008	0.011	0.012	0.017	0.040

for 0.5 h. Then the IR cell was evacuated for 0.5 h before recording the IR spectra.

The amount of coke deposited on the catalysts after a reaction at 723 K for 5 h was determined under an oxygen flow with a TA 2050 thermogravimetric analyzer.

2.3. Catalytic reaction

The skeletal isomerization of 1-butene was carried out in a continuous flow microreactor at atmospheric pressure [12]. The sample was heated to the reaction temperature of 823 K in flowing Ar, then a reactant stream with a fixed Ar/1-butene molar ratio of 4.9 (1-butene partial pressure of 31.5 kPa) was passed over the sample. The products were analyzed with an on-line Varian Aerograph 1420 TCD-GC equipped with a sebaconnitrile column.

2-butenes were not considered as products, since the double-bond isomerization between 1-butene and 2-butenes is very fast and 2-butene can also be converted into isobutene. The conversion of 1-butene and the selectivity to isobutene were determined as follows:

conversion (mol%)

= (moles of products except 1-butene and 2-butenes /moles of 1-butene fed) × 100,

selectivity (mol%)

= (moles of isobutene produced/moles of products except 1-butene and 2-butenes) × 100.

3. Results

Figure 1 shows the conversion of 1-butene and the selectivity to isobutene in the skeletal isomerization of 1-butene after a 50 min reaction in the temperature range of 573–823 K. Conversions of 1-butene over Al_2O_3 and F(0.008)/Al_2O_3 catalysts increase with an increase in the reaction temperature, while the selectivities to isobutene were the highest, at 723 K over both catalysts. When the reaction temperature is higher than 723 K, the selectivity to isobutene becomes low, due to an increase in cracking products of butene oligomers like C_2, C_3 and C_{5+} hydrocarbons. Similar trends in the conversion and selectivity are observed over F(0.04)/Al_2O_3 catalysts, although selectivity is very low.

The conversions and selectivities to isobutene at 723 K with different loading levels of fluorine on alumina catalyst are shown in figure 2. The conversion increases with

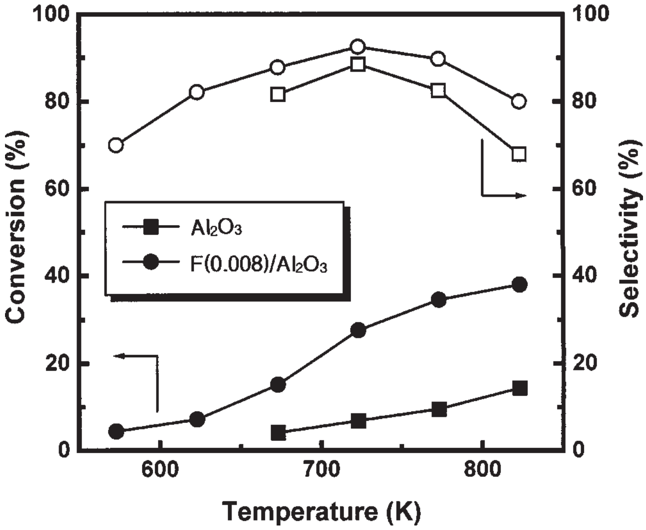

Figure 1. The skeletal isomerization of 1-butene over Al_2O_3 and F(0.008)/Al_2O_3 catalysts at various temperatures. $P_{\text{1-butene}} = 31.5$ kPa, WHSV = 3.1 h^{-1}.

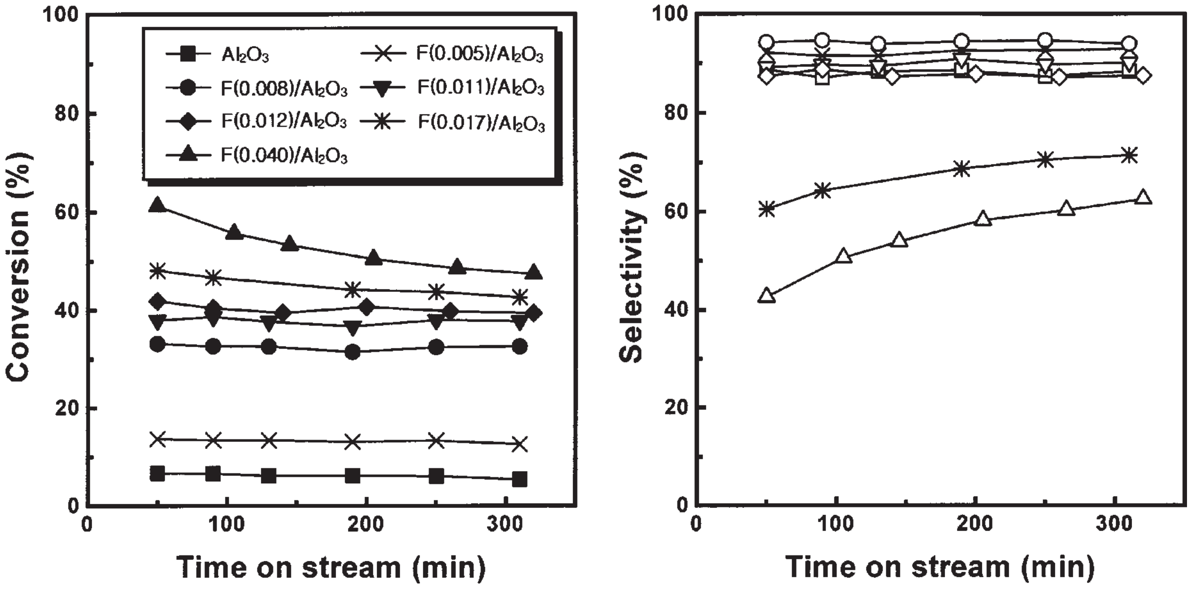

Figure 2. The time dependences in the conversions and the selectivities to isobutene in the skeletal isomerization over fluorine-modified catalysts. Reaction temperature = 723 K, $P_{\text{1-butene}} = 31.5$ kPa, WHSV = 3.1 h^{-1}.

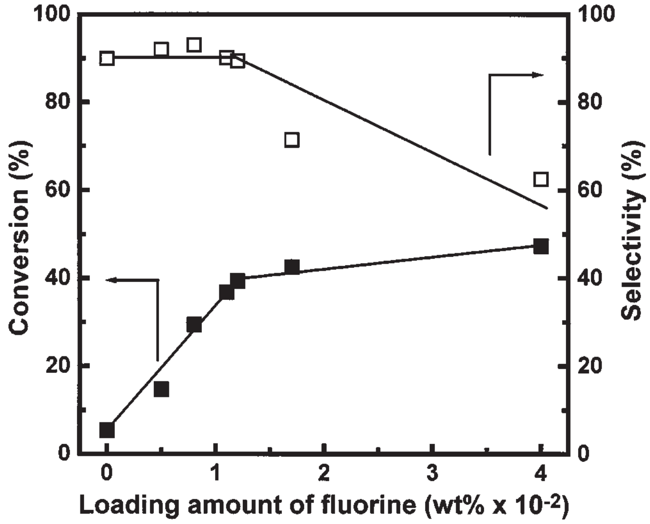

Figure 3. The variations of the conversions and the selectivities to isobutene in the skeletal isomerization of 1-butene with loading level of fluorine. Reaction temperature = 723 K, $P_{1\text{-butene}}$ = 31.5 kPa, WHSV = 3.1 h^{-1}.

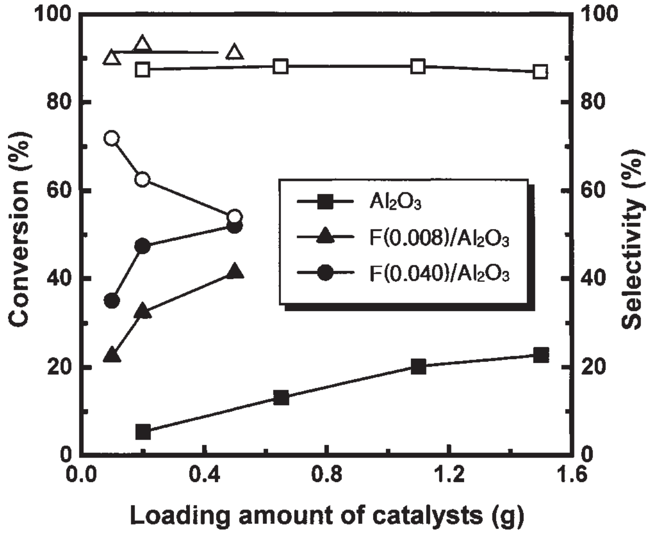

Figure 4. The variations of the conversion (full) and the selectivity to isobutene (open) over Al_2O_3, F(0.008)/Al_2O_3 and F(0.040)/Al_2O_3 catalysts with various amounts of catalyst loadings. Reaction temperature = 723 K, $P_{1\text{-butene}}$ = 31.5 kPa, WHSV = 3.1 h^{-1}.

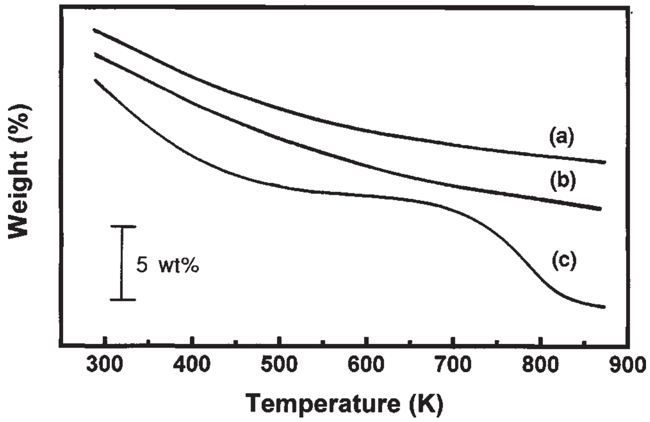

Figure 5. TG curves of used Al_2O_3 (a), F(0.008)/Al_2O_3 (b) and F(0.040)/Al_2O_3 (c) catalysts for 5 h and 723 K. $P_{1\text{-butene}}$ = 31.5 kPa and WHSV = 3.1 h^{-1}.

an increase in the loading level of fluorine. F(0.04)/Al_2O_3 catalyst with a high level of fluorine loading shows the highest conversion, while the conversion of Al_2O_3 catalyst without fluorine loading shows the lowest conversion. On the other hand, the opposite was observed for selectivity to isobutene. The selectivities of catalysts with low loadings of fluorine such as F(0.005)/Al_2O_3, F(0.008)/Al_2O_3, F(0.011)/Al_2O_3 and F(0.012)/Al_2O_3 are high, but those of F(0.017)/Al_2O_3 and F(0.040)/Al_2O_3 catalysts low.

Another difference in the conversion and the selectivity with the loading level of fluorine is the time dependence. The conversion and the selectivity change with a reaction time over F(0.017)/Al_2O_3 and F(0.040)/Al_2O_3 catalysts with high levels of fluorine loading. By contrast, the conversions and the selectivities are almost constant with reaction time for Al_2O_3, F(0.005)/Al_2O_3, F(0.008)/Al_2O_3, F(0.011)/Al_2O_3 and F(0.012)/Al_2O_3 catalysts with low loading levels of fluorine. A significant decrease in the conversion and an increase in the selectivity are observed on the catalysts with high loading of fluorine, but there are no changes in the conversion and selectivity on the catalysts with low loadings.

The dependences of the conversion and the selectivity to isobutene with the loading level of fluorine is shown in figure 3. This summarizes the reaction results at 723 K after 5 h on stream. The selectivity is very high for catalysts with low loadings of fluorine. The conversion apparently increases with loading amounts of fluorine below 0.012 wt%. However, conversion increases only a bit, but the selectivity decreases drastically above the fluorine loading of 0.012 wt%. The changes of the conversion and the selectivity are considerably different at the border of fluorine loading of 0.012 wt%.

The conversion and the selectivity to isobutene also vary with the amount of catalyst used in the reaction as shown in figure 4. The selectivities of Al_2O_3 and F(0.008)/Al_2O_3 catalysts do not change with catalyst amount, while that of F(0.040)/Al_2O_3 catalyst decreases. The selectivities of the catalysts with low levels of fluorine loading are constantly high irrespective of the conversion or the amount of catalyst. On the other hand, the selectivities of the catalysts with high levels of fluorine loading decrease with an increase in the catalyst amount. This difference shows that the preferable reactions of fluorine-modified alumina catalysts are different with the loading level of fluorine.

Figure 5 shows the results of the TG analysis at a range of 303–873 K under an oxygen atmosphere for catalysts after a reaction at 723 K for 5 h. The weight loss is different for the loading level of fluorine. The weight loss is high above 673 K for used F(0.040)/Al_2O_3 catalysts, while the weight losses are negligible for Al_2O_3 and F(0.008)/Al_2O_3 catalysts. The weight loss above 673 K reflects the amount of deposited carbon [22] burned in an oxygen atmosphere. The amount of carbon deposition on the F(0.040)/Al_2O_3

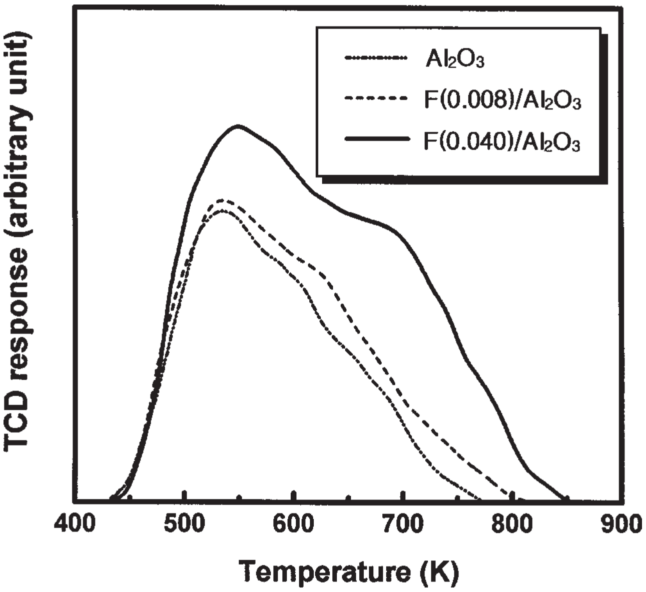

Figure 6. Ammonia TPD profiles from Al_2O_3, F(0.008)/Al_2O_3 and F(0.040)/Al_2O_3 catalysts.

catalyst showing the low selectivity to isobutene is much larger than those on Al_2O_3 and F(0.008)/Al_2O_3 catalysts with high selectivity. The low amount of carbon deposition on the isobutene selective catalysts indicates that there is no high boiling intermediate formed in the skeletal isomerization.

The profiles of NH_3-TPD are distinct from the loading level of fluorine on alumina. Figure 6 shows that the amount of ammonia desorbed above 673 K in the profiles of NH_3-TPD increases with an increase in the loading level of fluorine. It can be understood that the number of strong acid sites on the catalysts increases with fluorine loading.

Figure 7 shows the adsorption–desorption behavior of 1-butene investigated using the gravimetric adsorption apparatus. 1-butene is not only adsorbed a little over Al_2O_3 and F(0.008)/Al_2O_3 catalysts at 300 K, but also desorbed quickly even by evacuation. On the other hand, a large amount of 1-butene is adsorbed on F(0.040)/Al_2O_3 catalyst and some 1-butene is retained after evacuation at 300 K. The variation of the amount and the reversibility of 1-butene adsorption with loading level of fluorine reflect differences in the adsorbed states of 1-butene on F(0.008)/Al_2O_3 and F(0.040)/Al_2O_3 catalysts.

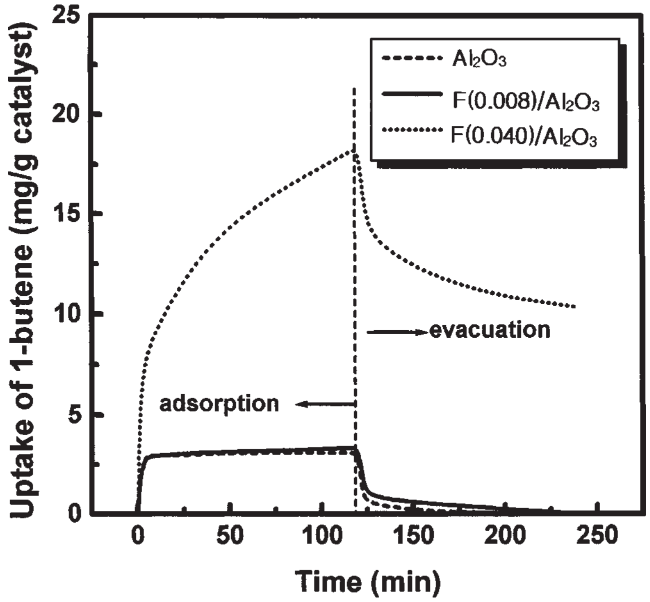

Figure 7. Adsorption–desorption behavior of 1-butene over Al_2O_3, F(0.008)/Al_2O_3 and F(0.040)/Al_2O_3 catalysts at 300 K. Catalysts are exposed to 30.4 kPa of 1-butene during the adsorption process.

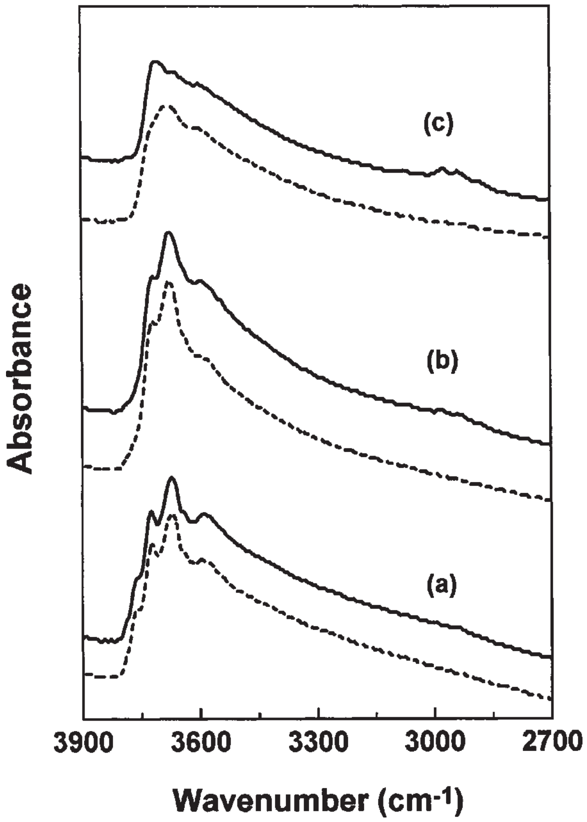

Figure 8. IR spectra of (a) Al_2O_3, (b) F(0.008)/Al_2O_3 and (c) F(0.040)/ Al_2O_3 catalysts before (- - -) and after (—) exposure to 1-butene vapor at 723 K.

Figure 8 shows the IR spectra in the O–H and C–H region of the catalysts exposed to 1-butene vapor followed by evacuation at 723 K. Three absorption bands were observed at 3578, 3683 and 3729 cm^{-1} on the catalysts of Al_2O_3 and F(0.008)/Al_2O_3 by the evacuation of 723 K. The absorption band at 3578 cm^{-1} is due to OH groups by the strong adsorption of water molecules. At 3683 cm^{-1} there are acidic OH groups and at 3729 cm^{-1} there are terminal acidic OH groups [23]. The intensities of the absorption bands at 3578 and 3689 cm^{-1} on F(0.040)/Al_2O_3 are very weak, and these at 3729 cm^{-1} are observed at 3699 cm^{-1}. This can be attributed to the decrease in the number of terminal OH groups on alumina surfaces which is caused by fluorine modification. The absorption bands of hydrocarbons on fluorine-modified catalysts are observed after exposure to 1-butene. But those on Al_2O_3 and F(0.008)/Al_2O_3 catalysts are easily diminished by evacuation. On the other hand, absorption bands at 2878, 2936 and 2974 cm^{-1} are still observed on F(0.040)/Al_2O_3 catalysts exposed to 1-butene and after evacuation for 30 min. The absorption bands at 2878 and 2936 cm^{-1} are assigned to –CH stretching of –CH_3 and/or –CH_2 groups in aliphatic compounds, and those at 2974 cm^{-1} are caused by =CH stretching in unsaturated hydrocarbon compounds [24]. The absorption bands due to the adsorption of 1-butene remain largely on F(0.040)/Al_2O_3 catalysts even after evacuation, while they are faintly observed after evacuation on F(0.008)/Al_2O_3 catalysts. Although it is difficult to deduce the adsorbed form of 1-butene from this finding, it is clear that the adsorbed state of 1-butene differs with the loading level of fluorine. This suggests that 1-butene may be adsorbed on F(0.040)/Al_2O_3 catalysts of considerable strength or in an oligmerized state with low vaporizability, resulting in slow desorption.

4. Discussion

The selectivity to isobutene, which was produced through the skeletal isomerization of 1-butene, depends considerably on the loading level of fluorine. The selectivity is high and constant for catalysts with fluorine loading levels up to 0.012 wt% and the increase in the loading level of fluorine gives an increase in the conversion of 1-butene. In contrast, with an increase in the loading level of fluorine the conversion increases but the selectivity decreases when the loading level of fluorine exceeds 0.017 wt%. The deactivation behavior also varies with a loading level of fluorine below 0.012 wt% and above 0.017 wt% as well as the selectivity to isobutene. The conversions and selectivities are constant with a given reaction time, as shown in figure 2, over the catalysts with low levels of fluorine loading. With respect to the catalysts with high levels of fluorine loading, the conversion decreases and the selectivity increases as the reaction proceeds. The catalysts with low levels of fluorine loading had a selectivity that was constant, regardless of the amount of catalyst, as shown in figure 4. Otherwise, the selectivity becomes low over the catalysts with high levels of fluorine loading with an increase in the catalyst amount. The fact that the relationship between the conversion and selectivity is different with the loading level of fluorine. Since there is an equilibrium limitation on the composition between butenes, the conversion does not exceed 38.5% at 723 K if only skeletal isomerization occurs. The fact that increasing conversion with decreasing selectivity is observed with catalysts with high levels of fluorine loading, indicating that the acceleration of the oligomerization followed by cracking to produce C_2, C_3 and C_5^+ hydrocarbons as well as skeletal isomerization occur simultaneously.

The variations of the conversion and selectivity to isobutene with catalyst amounts also support the above mentioned difference due to the loading level of fluorine. The selectivity is constantly high over the catalyst with low levels of fluorine loading irrespective of the catalyst amount, while the conversion becomes high but the selectivity decreases over the catalyst with high levels of fluorine loading. Since there is a limit of the selectivity to skeletal isomerization, the conversion increases on the catalyst with high levels of fluorine loading due to oligomerization followed by cracking, resulting in a decrease in selectivity.

The adsorption–desorption behavior of 1-butene molecules on the fluorine-modified catalysts is also considerably different with loading levels of fluorine from the IR absorption spectra and the adsorption–desorption measurements. The absorption bands of hydrocarbons are still observed on catalysts with high levels of fluorine loading after exposure to 1-butene followed by evacuation. In contrast, the adsorbed amounts of 1-butene molecules on Al_2O_3 and F(0.008)/Al_2O_3 catalysts measured in the adsorption–desorption investigation are small and are easily desorbed by evacuation. However, a lot of 1-butene molecules are adsorbed on the F(0.040)/Al_2O_3 catalyst and remained even after evacuation. The catalysts with low levels of fluorine loading, such as Al_2O_3 and F(0.008)/Al_2O_3, have low concentrations of strong acid sites (figure 6), therefore 1-butene molecules adsorb distantly resulting in fast desorption. Opposite to this, 1-butene molecules adsorbed on F(0.040)/Al_2O_3 catalysts with high concentrations of strong acid sites do not desorb completely. Since the boiling point of 1-butene is 267 K, the slow desorption of adsorbed 1-butene molecules at 298 K suggests that 1-butene is not adsorbed solely but is adsorbed in an oligomeric form or in an aggregated state with intermolecular interaction.

TG analyses of the used catalysts support this explanation. The amount of carbon deposition is considerably high on F(0.040)/Al_2O_3 catalysts with high levels of fluorine loading due to adsorption of 1-butene in an oligomeric or aggregate form. Since a dimer or trimer is an essential intermediate to form C_2, C_3 and C_{5+} hydrocarbons and the formation of these hydrocarbons reduces the selectivity to isobutene, the low selectivity on F(0.040)/Al_2O_3 catalysts is due to easy formation of oligomer. Negligible amounts of carbon deposition on the catalysts with low levels of fluorine loading indicate the low possibility of the formation of oligomers and the high selectivity for skeletal isomerization. From these findings, the adsorbed state of 1-butene molecules depends on the concentration of the strong acid site influenced by the loading level of fluorine.

There was a doubt on the monomolecular skeletal isomerization because of a high activation energy due to C–C bond breakage [25]. Later, quantum mechanical calculations and IR studies got rid of such prejudice [12,20]. Therefore, if we accept that the skeletal isomerization is mainly carried out by the monomolecular reaction, the selectivity change with the loading level of fluorine is easily related to differences in the adsorbed state of 1-butene molecules. The increase in the concentration of the strong acid site with increase of fluorine loading induces the close location of activated butene molecules on the catalyst surface, catalyzing the bimolecular reaction to produce cracked products. Since the equilibrium limitation on cracking is not severe compared to skeletal isomerization, the conversion increases but the selectivity to isobutene decreases. On the other hand, the monomolecular skeletal isomerization is preferable on the catalyst with low levels of fluorine loading due to its low concentration of strong acid sites. The selectivity is high but the conversion is low, because the number of active sites is small and the conversion is limited by equilibrium.

Seo et al. [12] suggested that the high selectivity for skeletal isomerization is due to distant location of adsorbed butene molecules by restriction of the pore structure, from the simulated distribution of butene molecules in the pores of FER and MFI zeolites. According to this point of view, the solely adsorbed 1-butene due to the low concentration of strong acid site is a plausible reason for the high selectivity of alumina catalysts with low levels of fluorine loading. Likewise, the low selectivity to isobutene, the fast deactivation due to carbon deposition, and irreversible adsorption of 1-butene on F(0.040)/Al_2O_3 catalysts of high concentration of strong acid sites are caused by the oligomeric adsorbed state, with preference to the bimolecular reaction and producing high boiling materials easily converted to deposited carbon.

Since alumina has various sizes of pores, it is not easy to relate the loading level of fluorine to the surface density of acid sites. The calculation for the effective distance to suppress the dimerization of activated butenes also has many difficulties. But the distant location of activated butenes is plausible as the basic reason for the high selectivity to isobutene not only for fluorine-modified aluminas, but also for zeolites. The restriction of FER zeolite pores inhibits close location of activated butene molecules and the low concentration of strong acid sites of amorphous catalysts induces the distant location of adsorbed butene molecules to suppress oligomerization, resulting in high selectivity to skeletal isomerization.

5. Conclusions

The selectivity for skeletal isomerization of 1-butene on the fluorine-modified alumina catalysts depends considerably on the loading level of fluorine. The conversion of 1-butene is low but the selectivity to isobutene is high over the catalysts with fluorine loadings less than 0.012 wt%. On the other hand, the conversion becomes high and the selectivity low on the catalysts with fluorine loading larger than 0.017 wt%. On the catalysts with high levels of fluorine loading, bimolecular oligomerization followed by cracking prevails due to the close location of activated butene molecules because of its high concentration of strong acid sites. Otherwise, the high selectivity to isobutene is observed on catalysts with low levels of fluorine loading, because the dimerization is suppressed by distant location of activated butene molecules due to low concentration of strong acid sites. The variations in the adsorbed amounts and the adsorption–desorption reversibility of 1-butene with the loading levels of fluorine are also caused by differences in the preference for oligomer formation. The distant location of activated butene molecules is suggested to be a basic reason for selective catalysts in skeletal isomerization regardless of the type, such as zeolites or amorphous catalysts.

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