Skeletal isomerization of 1-butene over mesoporous materials

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On the skeletal isomerization of 1-butene, mesoporous materials with mesopores too large to expect any shape selectivity have been used in order to investigate the effects of the concentration of acid sites on the conversion of 1-butene and the selectivity for isobutene. The concentrations of acid sites can be varied through the control of the Si/Al ratio. The conversion of 1-butene increases with increasing the aluminium content of mesoporous materials, while the selectivity for isobutene decreases. The results of ammonia TPD, IR measurement of 1-butene adsorption, and TG analysis of used catalysts indicate that distant location of activated 1-butene molecules induces the monomolecular reaction over the mesoporous materials with low aluminium content, resulting in high selectivity for skeletal isomerization. On the mesoporous material with high aluminium content, however, the high concentration of activated 1-butene molecules accelerates the multimolecular oligomerization and, thus, reduces the selectivity.

Keywords: 1-butene, skeletal isomerization, mesoporous material, acid site concentration, monomolecular reaction

1. Introduction

Skeletal isomerization of n-butenes to isobutene over acid catalysts is an attractive research topic because of the distinct difference in the selectivity along catalysts, as well as the economic value due to the effective use of C_4-raffinates. Though n-butenes can be converted to various hydrocarbons through isomerizations and the oligomerization followed by cracking, the high selectivities to isobutene over FER zeolite [1–3], fluorinated alumina [3–7], tungsten oxide supported on alumina [8], and alkali-modified silica–alumina [9] are very specific. Furthermore, it is also interesting that MFI zeolite [2,3,10] and unmodified silica–alumina [9,11] show very poor selectivity for isobutene. It is generally acceptable to use zeolite catalysts to explain the difference in the selectivity by pore structure, but it is not proper for amorphous catalysts such as alumina, silica–alumina and mesoporous material. Acidity is a plausible explanation for the difference in the selectivity, but the changes in the acidities of the FER and MFI zeolites do not entirely influence the selectivity [10].

Since there is an equilibrium limitation to the conversion of n-butenes to isobutene, the selectivity for the skeletal isomerization depends strongly on the extent of reactions producing C_2, C_3 and C_5^+ hydrocarbons. The high selectivity for isobutene is possible when oligomerization of butenes, followed by cracking, is highly suppressed. Therefore, the suppression of the reaction forming dimer, trimer or oligomer among activated butenes enhances the selectivity. The lowering of the partial pressure of butenes, in reactant stream or by shortening the contact time, is effective in increasing the selectivity for isobutene.

Molecular simulations of 1-butene adsorption show that the 1-butene molecules adsorbed in FER zeolite are distributed distantly in pores due to its specific pore structure, while the 1-butene molecules on MFI zeolite are adsorbed closely in MFI zeolite pores [10]. Based on the distribution of 1-butene in zeolite, we suggested that the high selectivity for isobutene on FER zeolite was due to the suppression of dimerization of activated butenes. The exceptional selectivity over fluorinated alumina with a low level of fluorine loading is also explained by the suppression of oligomer formation [7]. The fluorinated alumina with low fluorine loading shows a considerably high selectivity, but the fluorinated alumina with high fluorine loading has poor selectivity. The high concentration of a strong acid site on the fluorinated alumina accelerates multimolecular reactions and produces oligomers cracked to various hydrocarbons.

Mesoporous material has uniform pores too large to show any shape selectivity in the skeletal isomerization of n-butenes, but its acid site concentration can be easily controlled by the aluminium content. The pore diameter is about 40 Å, and thus the interaction between acid sites on the other side wall is negligible compared to the case of zeolite. Therefore, mesoporous materials with various aluminium contents are useful in investigating the effect of acid site concentration on the selectivity for isobutene. Though there are several mesoporous materials with different structures such as MCM-41 [12], MCM-48 [13] and KIT-1 [14], KIT-1 mesoporous material, as reported by Ryoo and Kim [14], is adequate for this study because of its facility in the incorporation of aluminium in the framework [14] and its high stability in the face of hydrothermal treatment [15].

In this paper, we report the variation of the selectivity for the skeletal isomerization with the concentration of

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acid sites on MCM-41 and KIT-1 mesoporous materials with various aluminium contents. The differences in the coke deposition and the adsorption–desorption behavior of 1-butenes along the aluminium content relating to the selectivity for isobutene are also discussed.

2. Experimental

2.1. Catalyst preparation

The hydrothermal syntheses of MCM-41 mesoporous materials with various aluminium contents were carried out at 373 K using the gel with the molar composition of $6.0SiO_2 : xAl_2O_3 : 1.5Na_2O : 0.15(NH_4)_2O : 1.0C_{16}H_{33}(CH_3)_3NCl$ (HTACl) : $220H_2O$, following the procedure of Ryoo and Kim [16]. HTACl (Aldrich, 25%) was used as a template and Ludox HS40 (Du Pont, 39.5% SiO_2) as a silica source. Sodium aluminate (Junsei Chemical Co., 80%) was added to the reactant mixture as an aluminium source, and the added amount was varied to get proper Si/Al ratios of synthesized mesoporous material. The reaction mixture was heated to 373 K for 24 h and then cooled to room temperature. Acetic acid was added by drops under vigorous stirring until the pH became 11.0. This mixture was heated again to 373 K for 24 h. The pH adjustment and subsequent heating were repeated two more times. The crystallized product was filtered, washed and dried. To remove surfactant, the dried mesoporous material was calcined at 823 K for 8 h. Ammonium ions were exchanged with a 0.5 N ammonium nitrate (Junsei Chemical Co., 98%) solution. H-form MCM-41 mesoporous materials were obtained by the calcination in air stream at 823 K for 8 h.

KIT-1 mesoporous materials with various aluminium contents were synthesized following the method developed by Ryoo and Kim [14] from gel compositions of $6.0SiO_2 : xAl_2O_3 : 3.5Na_2O : 0.15(NH_4)_2O : 1.0$HTACl : $4.0Na_2$EDTA : $350H_2O$ at 373 K. H-form KIT-1 mesoporous materials were prepared by a method similar to that for H-form MCM-41 mesoporous materials, except that the pH was adjusted to 10.2 by acetic acid.

2.2. Characterization of mesoporous material

The Si/Al ratios of synthesized mesoporous materials were determined by ICP (inductively coupled plasma, Jobin Yvon Co., JY. 38 plus) after digestion of the samples using aqueous hydrofluoric acid. The Si/Al ratios of the three MCM-41 catalysts were 102, 124 and 223 and were denoted as MCM-41( ). The ratio was written in the parentheses. Four KIT-1 mesoporous materials were obtained with Si/Al ratios of 14, 40, 54 and 97.

X-ray diffraction patterns were recorded using a X-ray diffractometer (Rigaku, D/MAX-1200) with Cu Kα X-ray and Ni filter at 35 kV and 15 mA.

Nitrogen adsorption isotherms on samples were obtained using a conventional volumetric adsorption system at liquid-nitrogen temperature after evacuation at 573 K for 2 h under vacuum.

^{27}Al magic-angle spinning (MAS) NMR spectra were obtained by using a Brucker AM 300 instrument with a relaxation delay of 5 s. Samples were spun with 3.5 kHz.

Temperature-programmed desorption (TPD) profiles of ammonia from mesoporous materials were recorded from 423 to 873 K with ramp rate of 10 K/min under a helium flow of 200 ml/min after activation in a He stream at 823 K for 2 h. Ammonia was fully adsorbed on the sample at 423 K by adding pulse of ammonia. The sample was then purged in a He stream at the same temperature for 2 h in order to eliminate physisorbed ammonia. The amount of ammonia desorbed from the sample was determined with a thermal conductivity detector (TCD).

The adsorption–desorption behaviors of 1-butene on mesoporous material with various aluminium contents were examined by FT-IR (ATI Mattson, Genesis series) with an *in situ* quartz cell at a resolution of 4 cm^{-1}. A self-supporting wafer of a 10 mg catalyst was evacuated under a vacuum of 2×10^{-4} Torr at 823 K for 1 h and exposed to 10 Torr of 1-butene at 723 K for 30 min. The sample was then evacuated at 723 K before recording the IR spectra.

The weight loss of the used catalyst was recorded under an oxygen flow with a thermogravimetric analyzer (TA Instruments, TGA 2050) to compare the amount of carbon deposit. The temperature was increased from 303 to 873 K with a ramp rate of 5 K/min.

2.3. Catalytic reaction

The skeletal isomerization of 1-butene was carried out using a conventional continuous-flow microreactor loaded with 0.2 g of mesoporous material at atmospheric pressure [2]. The sample was heated to 823 K for 2 h under an argon flow to activate the catalyst. Reaction temperature was set at 723 K and the reactant stream, with an argon/1-butene molar ratio of 4.9, was passed over the catalyst (1-butene partial pressure of 31.5 kPa). The reaction products were analyzed by an on-line gas chromatograph (Varian Aerograph 1420) equipped with a sebaconnitrile column and a thermal conductivity detector. Conversion was calculated in terms of mole-percent of 1-butene consumed and selectivity for isobutene in terms of the yield of isobutene divided by the conversion of 1-butene. 2-butenes were not considered as products, since the isomerization between 1-butene and 2-butene is much faster than the skeletal isomerization and 2-butenes can also be converted into isobutene.

3. Results and discussion

3.1. Characterization of MCM-41 and KIT-1 mesoporous materials

The skeletal isomerization of 1-butene to isobutene is an acid-catalyzed reaction [11], so the conversion and the selectivity depend considerably on the acidity of the catalyst. Since the acid site of mesoporous material is formed at a Si–O–Al bond, the aluminium content corresponds to the amount of acid sites, unless there is a lack of nonframework aluminium. Therefore, a wide variance of the aluminium content is desirable to investigate the effect of the concentration of the acid site on the selectivity, but there is a limited range of aluminium content, because a large amount of aluminium incorporation to the mesoporous material framework weakens the structure stability [17,18].

Figure 1 shows the XRD patterns of the calcined MCM-41(102) and KIT-1(97) samples. The diffraction patterns, consisting of one major peak along with three small peaks on MCM-41(102), agreed well with those reported previously [13,16]. Also, the XRD patterns of the KIT-1 mesoporous material were in agreement with that reported by Ryoo and Kim [14]. The distinct peaks assigned to the (100) plane were observed clearly at 1.9° of 2θ. Small and broad peaks related to the short-range structure order were also observed at 3–5° of 2θ. As KIT-1 mesoporous material has a high stability compared to MCM-41 mesoporous material, we can easily synthesize the KIT-1 mesoporous materials with the wide range of Si/Al ratio from 14 to 97. On the other hand, the Si/Al ratios of MCM-41 mesoporous materials were very high, as much as 102, 124 and 223. The MCM-41 and KIT-1 samples prepared here exhibited similar XRD patterns to those MCM-41(102) and KIT-1(97) samples, as shown in figure 1.

The existence of mesopores in MCM-41 and KIT-1 mesoporous materials can be confirmed from the adsorption isotherm of nitrogen. As shown in figure 2, the nitrogen adsorption isotherms, with the characteristic stepped shape, indicate capillary condensation of nitrogen at mesopores on KIT-1 mesoporous materials. The nitrogen adsorption isotherms of MCM-41 mesoporous materials are similar to those of KIT-1 mesoporous materials. The adsorption amount of nitrogen on KIT-1(14) is low compared to other mesoporous materials prepared in this study. It is well known that the incorporation of a large amount of aluminium lowers the crystallinity of mesoporous material [17], so a piece of amorphous material including alumina or silica was involved in this sample.

^{27}Al MAS NMR spectra show the existence of amorphous alumina in KIT-1 mesoporous material. Two peaks at 55.6 and -1.5 ppm of the chemical shift were observed. The peak at 55.6 ppm is attributed to aluminium in a framework tetrahedral position. On the other hand, the peak at -1.5 ppm is characteristic of an octahedral coordination (figure 3). The fractions of nonframework aluminium are about 19, 15 and 7% for KIT-1(14), KIT-1(40) and KIT-1(54) mesoporous materials, respectively. Though

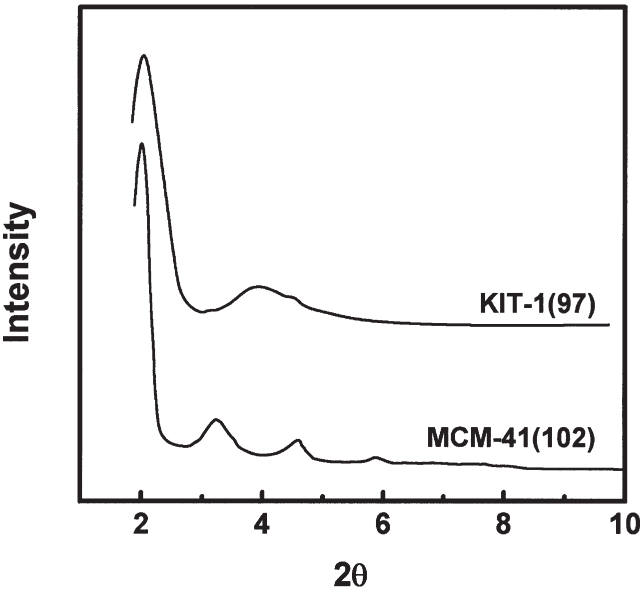

Figure 1. XRD patterns of MCM-41(102) and KIT-1(97) mesoporous materials.

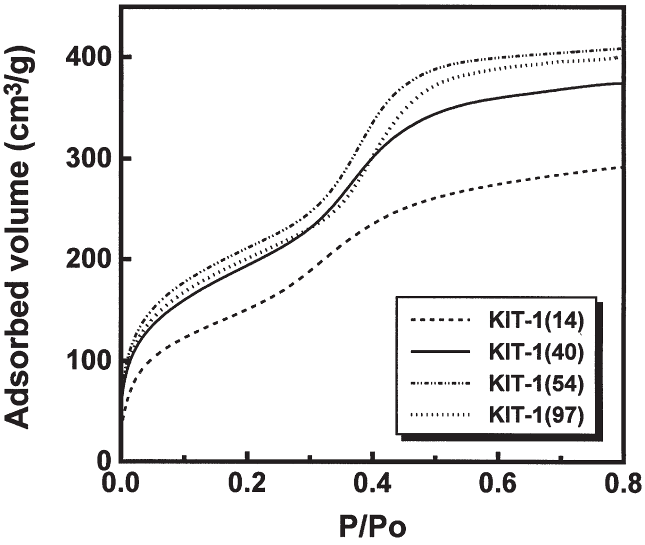

Figure 2. N_2 adsorption isotherms of KIT-1 mesoporous materials.

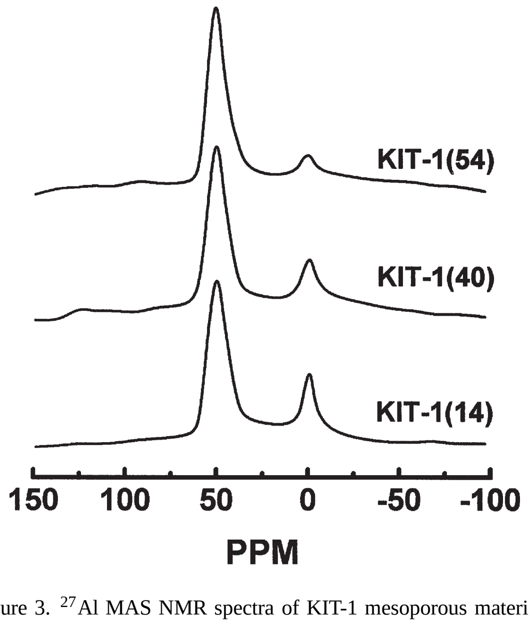

Figure 3. ^{27}Al MAS NMR spectra of KIT-1 mesoporous materials.

the content of amorphous material due to nonframework aluminium in KIT-1(14) mesoporous material is not high, about 19%, the coexistence of amorphous alumina is a plausible reason to reduce the crystallinity and the adsorption amount of nitrogen.

However, most of the aluminium in KIT-1 mesoporous material is incorporated in the framework and forms acid sites. This can be confirmed by the finding that the desorption amount of ammonia, indicating the number of acid sites, decreases with the increase in the Si/Al ratio, as shown in the ammonia TPD profiles of figure 4. The temperature at peak maximum does not change with the molar ratio of Si/Al ratio indicating no meaningful difference in acid strength. It is not completely correct to discuss the acidity of mesoporous material from TPD results only, but the increase in the concentration of acid sites with the increase in aluminium content is clear.

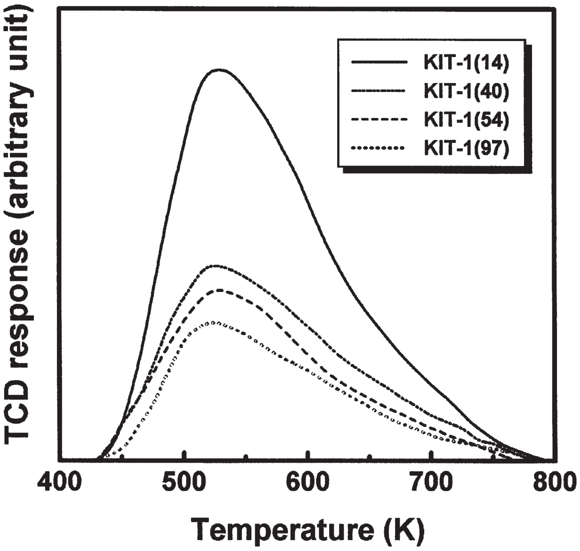

Figure 4. Ammonia TPD profiles from KIT-1 mesoporous materials.

3.2. Catalytic properties of MCM-41 and KIT-1 mesoporous materials

The skeletal isomerization of 1-butene over acid catalysts usually occurs accompanying oligomerization, followed by cracking and coke deposition. The conversion of 1-butene decreases according to the time on stream over ferrierite, while the selectivity for isobutene increases [2,19]. Based on this observation, Guisnet et al. suggested the alkyl radical on coke could work as an active site for the skeletal isomerization [20]. On the fluorinated aluminas, the lower selective catalyst to isobutene shows a faster deactivation due to coke deposit, indicating the selectivity for isobutene is not essentially related to the degree of deactivation [7]. Coke deposits enhance the selectivity of FER zeolite because of the increase of pore restriction, but it is not a fundamental factor in determining the selectivity. The preference to dimer formation, due to the high concentration of strong acid sites on the alumina with a high level of fluorine loading, is responsible for the coke deposits, rather than the skeletal isomerization, lowering the selectivity.

The decrease of the conversion and the increase of the selectivity according to the time on stream were observed on the KIT-1(14) catalyst, as shown in figure 5. But the KIT-1(54) and KIT-1(97) catalysts did not show any change in the conversion and the selectivity according to the time on stream, indicating that the deactivation is strongly related to the concentration of acid sites. The other observation deduced from figure 5 is the trend of the conversion and selectivity with the aluminium content. The selectivity for isobutene becomes high over KIT-1 catalysts with low aluminium contents, while the conversion becomes low. KIT-1 catalysts with a low concentration of acid sites show high selectivity and negligible deactivation. This means that selectivity and deactivation behaviors are strongly related to the concentration of acid sites.

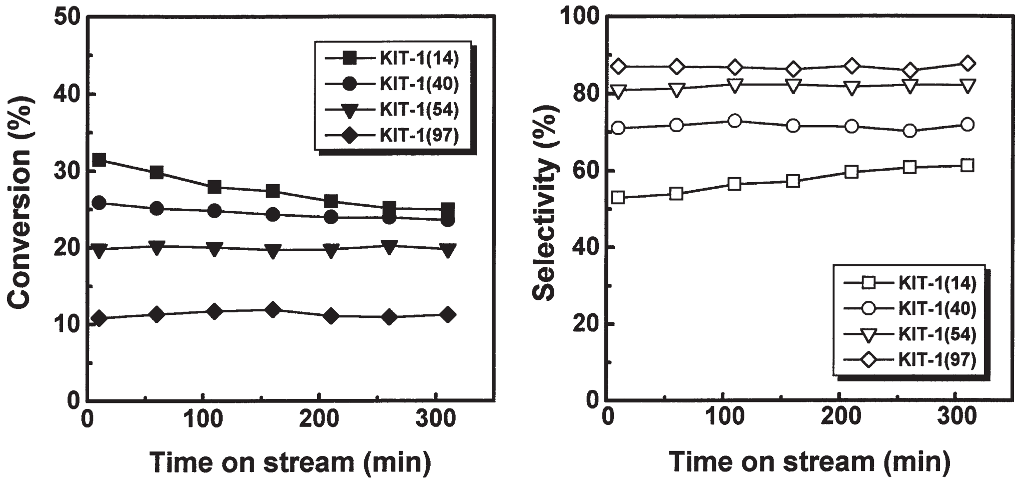

Figure 5. The time dependences in the conversions and the selectivities to isobutene in the skeletal isomerization of KIT-1 mesoporous materials. Reaction temperature = 723 K, $P_{1\text{-butene}} = 31.5$ kPa, WHSV = 3.1 h^{-1}.

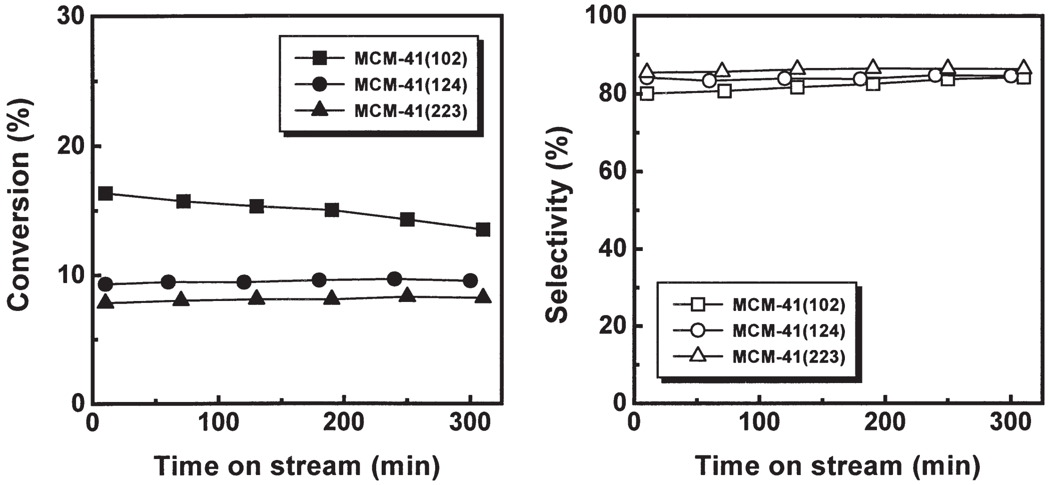

Figure 6. The time dependences in the conversions and the selectivities to isobutene in the skeletal isomerization of MCM-41 mesoporous materials. Reaction temperature = 723 K, $P_{1\text{-butene}} = 31.5$ kPa, WHSV = 3.1 h^{-1}.

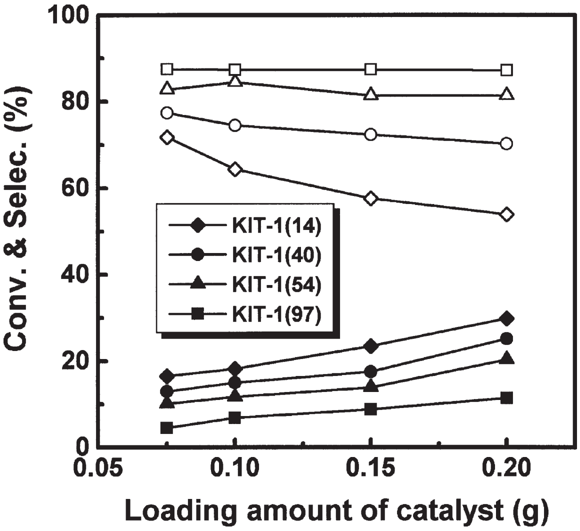

Figure 7. The variations of the conversions and the selectivities to isobutene in the skeletal isomerization of 1-butene with various amounts of catalyst loadings. Reaction temperature = 723 K, $P_{1\text{-butene}} = 31.5$ kPa, WHSV = 3.1 h^{-1}.

On the other hand, the selectivities for all MCM-41 catalysts used here have almost the same high value of 85%, as shown in figure 6. In the case of the MCM-41 catalyst, it is difficult to control the concentration of acid sites, because a small amount of aluminium is incorporated in the MCM-41 mesoporous material framework. Thus, we will discuss only the catalytic property of KIT-1 mesoporous material, because its Si/Al ratio varies in a wide range from 14 to 97, inducing differences in the selectivity and the conversion which are apparent.

The high selectivities of KIT-1(54) and KIT-1(97) catalysts are not ascribed to the low conversion. As shown in figure 7, the conversion increases with the loading amount of the catalysts, while the selectivities remain high. On the other hand, the KIT-1(14) catalyst with high aluminium content shows the decrease in the selectivity, with an increase in the loading amount of the catalyst. This means that the selectivity is determined essentially by the aluminium content, not by the conversion level of 1-butene.

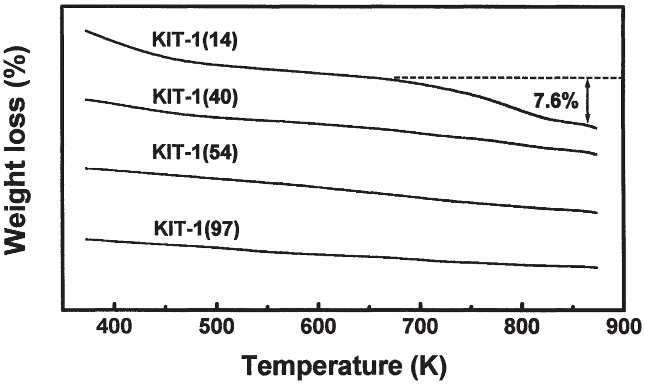

Figure 8. TG curves of used KIT-1 mesoporous materials for 5 h at 723 K.

Negligible change in the selectivity of KIT-1(54) or KIT-1(97) catalyst with time on stream is distinct from that of FER zeolite, which is a well known catalyst showing a high selectivity for isobutene [2,19]. The coke deposit on FER zeolite improves the selectivity, while the selectivity of the KIT-1 catalyst is not influenced by the coke deposit. However, the coke deposit on the KIT-1 catalyst varies with the aluminium content. The weight loss of used catalyst in oxygen flow above 673 K is significant on the KIT-1(14) catalyst, as shown in figure 8. The coke deposit is severe on KIT-1(14) catalysts with a high aluminium content, but it is negligible on KIT-1 catalysts with a low aluminium content.

The adsorption–desorption behavior of 1-butene was investigated using IR measurement. Figure 9 shows the IR spectra in the O–H and C–H region of the catalysts evacuated at 723 K for a given time followed by exposure to 10 Torr of 1-butene at 723 K for 30 min. 1-butene is desorbed quickly, even by evacuation for 5 min over KIT-1(97) catalyst. The absorption bands of 1-butene on KIT-1(54) catalyst were diminished by evacuation for 30 min. On the other hand, some 1-butene is retained even

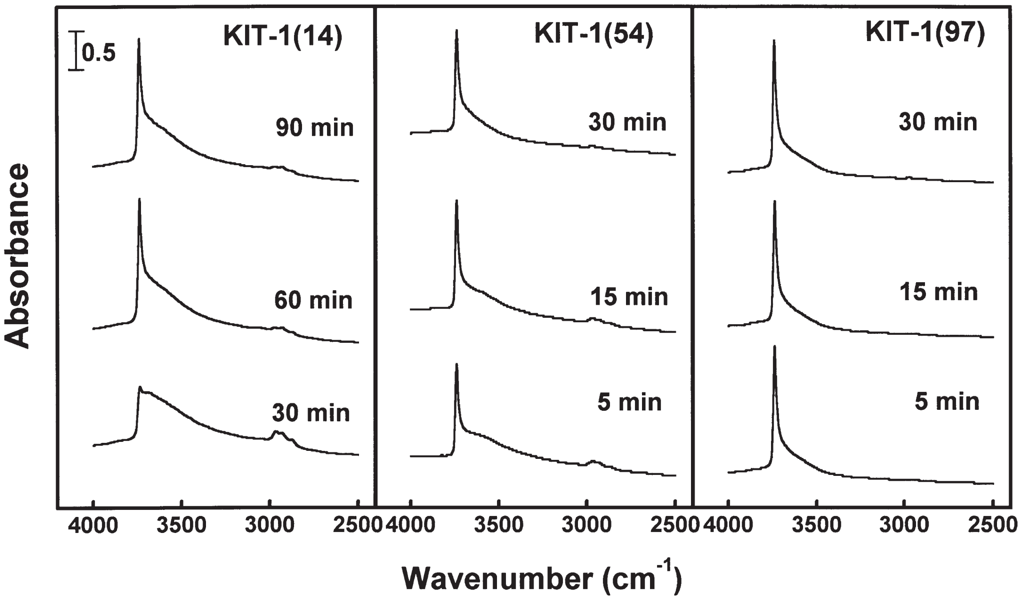

Figure 9. IR spectra of KIT-1 mesoporous materials before and after exposure to 1-butene vapor at 723 K.

after evacuation for 90 min over the KIT-1(14) catalyst. The variation of 1-butene retention with aluminium content of the KIT-1 catalysts reflects differences in the adsorbed states of 1-butene on KIT-1(14), KIT-1(54) and KIT-1(97) catalysts. These findings indicate that 1-butene may be adsorbed on a KIT-1(14) catalyst of considerable strength or in an oligomerized state with low vaporizability, resulting in slow desorption.

3.3. Cause for the high selectivity for isobutene over KIT-1 catalysts with low aluminium content

The selectivity for isobutene depends on the aluminium content of KIT-1 catalysts. The conversion increases with an increase in the aluminium content, but the selectivity decreases, as shown in figure 10. The deactivation behavior varies with the aluminium content, as does the selectivity for isobutene. The conversions and selectivities are constant with a given reaction time over the KIT-1 catalysts with low aluminium contents, as shown in figure 5. On the other hand, over KIT-1(14) catalyst with high aluminium content, the conversion decreases and the selectivity increases with time on stream. Furthermore, the selectivity becomes low upon increasing the amount of KIT-1(14) catalyst. The result of increasing conversion with decreasing selectivity is observed on the catalyst with high aluminium content, indicating that the oligomerization followed by cracking to produce C_2, C_3 and C_5^+ hydrocarbons is accelerated on the catalyst with a high concentration of acid sites.

The variations of the conversion and selectivity with the loading amount of catalysts also support the above mentioned difference due to the aluminium content. The selectivity is constantly high over the KIT-1 catalysts with low aluminium contents, irrespective of the catalyst amount, while the selectivity is low over the KIT-1(14) catalyst with high aluminium content.

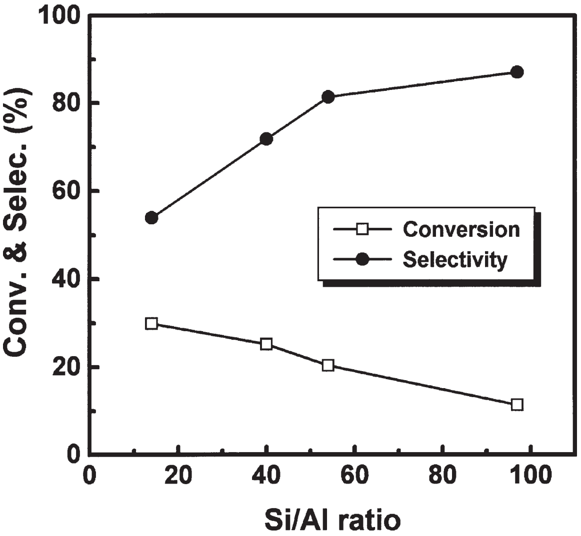

Figure 10. The variations of the conversions and the selectivities to isobutene in the skeletal isomerization of 1-butene with Si/Al ratio of KIT-1 mesoporous materials. Reaction temperature = 723 K, $P_{\text{1-butene}} =$ 31.5 kPa, WHSV = 3.1 h^{-1}.

The adsorption–desorption behavior of 1-butene from the IR absorption spectra over the KIT-1 catalysts with various aluminium contents is considerably different with aluminium content, as shown in figure 9. On the KIT-1(97) catalyst with low concentration of acid sites, 1-butene molecules desorb easily and completely by an evacuation for 5 min. However, 1-butene molecules adsorbed on a KIT-1(14) catalyst with a high concentration of acid sites cannot desorb completely. Since the boiling point of 1-butene is 267 K, the slow desorption of adsorbed 1-butene by the evacuation at 723 K for a time as long as 90 min suggests that 1-butene is not adsorbed solely but is adsorbed in an oligomeric form or in an aggregated state with intermolecular interaction.

The results of TG analysis support this suggestion (figure 8). The amount of carbon deposition is considerably high on the KIT-1(14) catalyst with a high aluminium content. Negligible amounts of carbon deposition on the KIT-1 catalysts with low aluminium content indicate the low possibility of the formation of oligomers, thus, the high selectivity for skeletal isomerization.

We suggested already that the high selectivity for skeletal isomerization is due to the 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 [9]. Furthermore, the result of FER zeolite is very similar to that for the alumina catalyst with low levels of fluorine loading reported previously [7]. The monomolecular skeletal isomerization is preferable on the alumina catalysts with low levels of fluorine loading, due to their low concentration of acid sites. Accordingly, the solely adsorbed 1-butene due to the low concentration of acid site is a plausible reason for the high selectivity of KIT-1 catalysts with low aluminium content. This suggestion is in nice accord with Houzvicka's work describing the role of density of acid sites [21].

From these findings, we conclude as follows: On KIT-1 catalysts with low aluminium content, the high selectivity for isobutene is observed, because the dimerization is suppressed by the distant location of 1-butene which is activated due to the low concentration of acid sites. This distant location of activated 1-butene molecules is responsible for the selectivity of the catalyst in the skeletal isomerization of 1-butene, regardless of whether it has uniform pores or not, such as zeolite, amorphous catalyst or mesoporous material.

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