Isomerization of $n$-butane over sulfated zirconia catalyst under supercritical conditions

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Abstract
Heterogeneous catalytic processes in the supercritical fluid offer environmentally benign alternatives to current catalyst technologies. In the case of isomerization of light alkanes over solid acid catalysts at atmospheric pressure, the catalysts deactivate rapidly due to coke formation on the catalyst surface. To solve this problem, the isomerization of $n$-butane over sulfated zirconia was studied in a $n$-butane supercritical condition of reactant and products. Under the supercritical condition, no significant deactivation was observed, and the steady state activity was maintained. Furthermore, the active sites of sulfated zirconia were characterized by FT-IR spectroscopy, and it was found that Lewis acid sites on sulfated zirconia play an important role in the isomerization of $n$-butane.

1. Introduction
With the recent enactment and phasing-in of regulations regarding the elimination of certain gasoline components such as benzene, aromatics, and olefins [1-2], there has been a great demand for both clean and high-octane gasoline components. Thus, $i$-butane is becoming an important compound as a feedstock for the alkylate gasoline, MTBE and ETBE. There are several reports that sulfated oxide catalysts can isomerize $n$-butane to $i$-butane even at room temperature. Sulfated zirconia in particular is known as a solid super acid and is a potential effective catalyst of the isomerization [3-16]. However, it is also known that strong acidity causes a rapid deactivation during isomerization of alkanes. Many of published data have suggested various reasons for the deactivation [17-20], but the prevailing theory is the coke formation on the catalyst surface [18-26]. Therefore, reduction of the coke formation during the reaction is the most important issue for a satisfactory the isomerization reaction.

Supercritical fluids have been widely studied as extraction media. Such a fluid behaves both as a liquid exhibiting high solubility and as a gas exhibiting sensitive density changes with the pressure and the temperature. Such properties lead to its
unique characteristics of low viscosity and high diffusibility. These characteristics promote the penetration into porous materials and material diffusion. Solubility of materials depends on not only the characters of molecules but also the distance between each paw of molecules; therefore, the density also plays an important role in the material solubility. Supercritical fluids have high density; such density can be easily controlled by the pressure and the temperature, i.e. solubility can be controlled [27]. We have previously reported our findings regarding solid acid-catalyzed alkylation of \textit{i}-butane with \textit{1}-butene under supercritical conditions; we found that coke formation on the solid acid catalysts was reduced and that the deactivation could be reduced under supercritical conditions [28].

We have applied a supercritical fluid to minimize the deactivation rate and to achieve stable activity on solid acid-catalyzed isomerization. We expect that the supercritical fluids would extract the coke precursors from the catalyst surface effectively, and that the initial catalytic activity would be maintained.

In this work, we have studied isomerization of \textit{n}-butane to \textit{iso}-butane over sulfated zirconia under supercritical conditions of reactants and products to investigate the influence of reaction conditions on the catalyst activity. We also characterized the acidic nature; the acidic nature of sulfated zirconia was investigated using FT-IR spectroscopy.

2. Experimental

2.1. Catalyst preparation

\textit{SO}_4^{2-}/\textit{ZrO}_2 (labeled as SZ) samples were prepared from zirconium hydroxide (Daiichi Kigenso Kagaku Kougyo, grade: RSD). Zirconium hydroxide was impregnated with (\textit{NH}_4)_2\textit{SO}_4 aqueous solution and stirred overnight at 333K. The solid catalyst obtained was dried up at 373K for 12 hours. The sulfur content ratio of samples was adjusted at 4.0 wt\%. Dried samples were calcined \textit{in-situ} prior to the reaction as described in 2.3.

2.2. Catalyst characterization

In order to study the acidity of the catalyst, IR spectra were taken. A vacuum-tight IR cell with KBr windows was designed to fit an infrared spectrometer (Shimadzu, FT-IR-8200PC) and was attached to a vacuum system (10^{-4}\text{Pa}). The cell was arranged such that the zeolite wafer (0.01 g cm^{-2}) could be set down into slots between the KBr windows, and pulled upward by a magnet into the heated part. The zeolite samples were calcined \textit{in-situ} for 5 hours at various temperatures following
with evacuation for 30 minutes at same temperatures. We also obtained the IR spectra with pyridine adsorption. The samples were cooled down to 373 K and were exposed to 670 Pa (5 Torr) of pyridine for 0.5. After evacuation for 0.5 h, the temperature was raised and IR spectra were taken at the corresponding temperatures. In order to study the crystal structures of SZ, XRD patterns of calcined SZ were obtained on an X-ray diffractometer (Rigaku, RINT2100V/P) with CuKα (λ=0.15418nm). To determine the specific surface area of the catalysts, nitrogen adsorption measurements were performed at 77 K on an automatic gas adsorption apparatus (BEL JAPAN, BELSORP 28SA). As pretreatment, 0.3 g of sample was placed in a Pyrex tube and evacuated at 573 K over night. The specific surface area was obtained by the BET method.

2.3. Isomerization of n-butane

Isomerization of n-butane was carried out in a fixed bed continuous flow reactor. The detailed reactor flow has been described in our previous paper [28]. The critical point of n-butane is at 425 K and 3.8 MPa [29]. The conditions of the reactions were as followed, reaction temperature; 388-588 K, reaction pressure; 0.1-6.0 MPa, the weight of the catalyst; 1.0 g, the feed rate of liquid n-butane; 0.25 ml min⁻¹. Prior to the reaction, the catalysts were pelletized, crushed to 30-50 mesh, and calcined in-situ at 673-973 K for 5 h under O₂ flow, then cooled down to the reaction temperature, and purged with He for 1 h. The product gas was analyzed by using an on-line TCD gas chromatograph (Shimadzu, GC-8A IT) equipped with a stainless column (GL Sciences, VZ-9, 6 m).

3. Results and discussion

3.1. Isomerization of n-butane under supercritical conditions

We studied the isomerization of n-butane at various conditions to verify the effect of the supercritical conditions. The conversion profiles are also shown as a function of time on stream under the condition of the gas-phase (0.1 MPa) and the supercritical condition (4.0 MPa) in Fig. 1. Under the gas-phase reaction, although initial catalytic activity was relatively high, rapid deactivation occurred and no activity was observed after 3 hours on stream. In the case of the reaction under the supercritical condition, the conversion rose from 20% up to 25% during the initial 2h, and it was maintained without any deactivation until the end of the reaction time. The lower initial catalytic activity of the reaction under the supercritical condition is due to the time required for establishing supercritical condition, and thus forming the coke precursor on the catalyst surface. The coke precursor is partly diffused after supercritical conditions is
established.

The influences of the reaction pressure on conversion, selectivity, and deactivation rate of the isomerization at 488 K are summarized in Fig. 2 (the reactions at the pressure above 3.8 MPa were supercritical phase). The conversion was measured after 6 h time on stream, and the deactivation rate is defined as following equation based on the results of the conversion:

\[
\ln C = -at + b
\]

(C: conversion; a: deactivation rate; t: time on stream; b: constant).

**Fig. 1** Catalytic activity over SO\textsubscript{4}\textsuperscript{2-}/ZrO\textsubscript{2} as a function of time on stream. Reaction conditions: 488 K, 0.1-6.0MPa, Catalyst: SZ 1.0g (Calcined at 773K), Feed rate of liquid n-butane: 0.25ml min\textsuperscript{-1}.

**Fig. 2** Conversion, selectivity and deactivation rate as a function of reaction pressure. Reaction conditions: 488 K, 0.2-6.0 MPa; Catalyst: SZ (Calcined at 773 K); WHSV: 9.6 h\textsuperscript{-1}.
Under the lower pressure gas-phase reaction around atmospheric pressure, the deactivation was so rapid that almost no activity was observed after 6 hours on stream. The deactivation rates were reduced with the increase of the pressure. Especially under the supercritical condition, the deactivation was minimized and the conversion was higher comparing with those obtained under non-supercritical conditions. We assume that \( n \)-butane with high density and diffusivity acted not only as a reactant, but also as an extraction medium of coke precursors, and kept the catalyst surface fresh during the reaction under the supercritical conditions. We have studied the alkylation of \( i \)-butane over sulfated zirconia under supercritical conditions and the same process with some metal promoter [28]. We obtained the result that the more the catalyst deactivated, the more the used catalyst lost its acid sites, specific surface area and pore volume due to the coke formation. In this study, it is indicated that the coke formation was reduced under the supercritical conditions, similarly in the case of the alkylation study. We also found that 4.0 MPa was the most favorable pressure with attention of the catalytic activities among our test conditions.

The influence of the reaction temperature was also studied at the pressure of 4.0 MPa, at which both high conversion and less deactivation rates were obtained (Fig. 3). Under the liquid phase reaction (below 425K), the deactivation rate was relatively high because of lower diffusibility. Furthermore, the catalytic activity was also lower because of lower reaction temperature. Under the supercritical conditions, the deactivation rate was reduced, but the deactivation rate increased as the reaction temperature was raised, especially above 500K. This rapid deactivation at higher temperature is assumed that the sub reaction becomes dominant above 500K. In order
to investigate the reason why the deactivation rate increased above 500K, we performed TGA of used CZ catalyst to compare the amount of coke formed on the used catalysts. In the TGA results, the catalyst after the reaction at the condition of 488 K (4.0 MPa) showed no weight loss due to the coke burn. On the contrary, the catalysts after the reactions at 538 K or 588 K(4.0 Mpa), showed weight losses corresponding to the coke that formed on the catalyst surface even though it is under the supercritical conditions. Therefore the rapid deactivation at higher temperature is assumed that the coke formation is promoted by the sub reactions i.e. cracking with main products of C2-C3. It is also concerned that at the constant pressure, the fluid density decreases as the temperature is raised because of lower diffusibility, which causes rapid deactivation. These occurrences of sub reactions and decrease of the diffusibility cause to form coke precursor and lead to rapid reactivation. Concerning of these result, both pressure and temperature are very important for this reaction.

As discussed above, the reaction conditions, i.e. the properties of the supercritical fluid are the important key for the reduction of the coke formation on the catalyst surface, and it was found that the condition slightly above the critical point showed a significant effect on the reaction stability.

3.2. Acidic nature of SO$_4^2-/ZrO_2$ for the isomerization of n-butane

Sulfated zirconia (SZ) is known as a catalyst which shows high conversion on the isomerization of alkanes, but the detailed structure of its active sites has not been elucidated completely. We have focused on the effect of calcination temperature of SZ and have investigated the relationship between its active site structure and the reaction activity.

<table>
<thead>
<tr>
<th>Calcination temp. /K</th>
<th>Specific surface area /m$^2$ g$^{-1}$</th>
<th>S content /wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>169</td>
<td>4.8</td>
</tr>
<tr>
<td>723</td>
<td>146</td>
<td>4.6</td>
</tr>
<tr>
<td>773</td>
<td>135</td>
<td>4.6</td>
</tr>
<tr>
<td>823</td>
<td>122</td>
<td>3.6</td>
</tr>
<tr>
<td>873</td>
<td>89</td>
<td>2.1</td>
</tr>
<tr>
<td>973</td>
<td>51</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* Determined by XRF

The surface properties of calcined SZ are listed in Table 1. BET results indicated that increasing calcination temperature causes the reduction of the specific
surface area of SZ. The decrease of the S concentration was observed at the high calcinations temperature, although there was no change of the S concentration at the calcinations temperature under 723K. In the TG curves of SZ, large amount of weight loss was detected around 800K. This weight loss is identified the deposition of sulfated groups, i.e. the reduction of the acid sites. We also studied the XRD patterns of SZ. The XRD pattern of SZ calcined at 673K showed broad peak, but SZ calcined at 723K and above shows tetragonal peaks of zirconia. Another peak was also obtained which was corresponding to monoclinic structure in the XRD patterns of SZ calcined above 823K. These facts indicate that 773K is the temperature that the zirconia is crystallized without sulfat e group decomposition. Under the temperature above 823K, both the crystallization to monoclinic structure and the decomposition of sulfate groups are accelerated with decreasing of surface area.

![Fig. 4 IR spectra of S=O stretching and O-H bending region of SO_4^2-/ZrO_2.](image)

The surface structure of SZ was studied by FT-IR spectroscopy (Fig. 4). At first, we obtained the IR spectra of SZ without calcinations, and consecutively obtained the spectra with increasing of temperature. At room temperature, there was only a broad peak around 1630 cm\(^{-1}\) assigned to the O-H bending mode of adsorbed water on the surface. But increasing of the temperature leads not only to the decrease of the O-H bending vibration but also to the appearance of the peak at 1360cm\(^{-1}\). This peak is
assigned to S=O asymmetric stretching vibration appeared after dehydration of adsorbed water. The peak of $\nu_{S=O}$ was decreased with increase of temperature, and completely disappeared above 673K. The peak of $\nu_{S=O}$ was shifted from 1360 cm$^{-1}$ to 1398 cm$^{-1}$ and became large up to 773 K as a result of dehydration. The main reason of this shift is assumed that the electron density of Zr was decreased due to the strong electronegativity of S=O after dehydration of water hydrated to sulfate groups.

Conversion and intensity of S=O in IR spectra as a function of calcination temperature of SZ are shown in Fig. 5. The reactions in this figure were carried out under supercritical conditions of $n$-butane (488 K and 3.8 MPa), and all samples showed no drastic deactivations during the reactions. The catalytic activity of SZ was greatly influenced by its calcination temperature. SZ calcined at 673 K was not reactive, but as the calcination temperature was raised, the SZ became active and the sample calcined at 773 K showed the best activity. The intensity of S=O was increased related to the catalytic activity. SZ calcined at 773K, which have high S=O electron density without decomposition of sulfate groups, showed high catalytic activity. Therefore the catalytic activity of this reaction is sensitive to the structure of sulfate gropes of the SZ.

In order to study the nature of acidity, pyridine (Py) was adsorbed as a probe molecule on the catalysts activated at each temperature and the adsorbed pyridine was observed by FT-IR (Fig. 6). The peak centered around 1445 cm$^{-1}$ is assigned to $19b$ band of the Py chemisorbed on Lewis acid sites (LPy) and the peak centered around 1541 cm$^{-1}$ is assigned to $19b$ band of the Py chemisorbed on Brønsted acid sites (BPy) [30-33]. The ratio of the amount of Brønsted acid sites to that of Lewis acid sites was estimated according to the literature [34]. As the calcination temperature of SZ was
raised, the amount of Brønsted acid sites decreased, and Brønsted acid sites completely disappeared at 973K. In the mean time, the amount of the Lewis acid sites increased up to the calcinations temperature of 773K and the Lewis acid sites decreased above 773K. The B/L ration was increase with the increase of the calcinations temperature. The amount of both Lewis and Brønsted acid sites were decreased with increase of calcination temperature because of the decomposition of sulfate groups. This result indicates that dehydration of SZ by calcination transforms Brønsted acid sites to Lewis acid sites. We assume that the water remained on the surface of SZ acted as Brønsted acid sites. Indeed, rehydration of pyridine-adsorbed SZ caused transformation of Lewis acid sites to Brønsted acid sites. From the results of IR spectroscopy, it is indicated that the calcination at high temperature removes the water adsorbed on the catalyst surface, and then the sulfate species begin to act as electron-attractive groups to express positive electron charge on a zirconium atom. As a result, the positive electron charge behaves as Lewis acid sites and the little water that remained on these sites behaves as Brønsted acid sites, as illustrated in Scheme 1 [b]. We found that 90% of the catalytic active sites of the SZ calcined at 773K were Lewis acidic sites. SZ samples calcined at 873-973 K, which were completely dehydrated and had only Lewis acidic sites as illustrated in Scheme 1[c], were also reactive for the isomerization of \( n \)-butane. These results indicate that the main active sites for this reaction are Lewis acid sites formed by calcination.

SZ calcined at 673 K contained had a larger amount of Brønsted acid sites and a smaller amount of Lewis acid sites than SZ calcined at 773 K. SZ calcined at 673K

![Fig. 6 IR spectra of pyridine adsorbed on SO\(_4^2\)/ZrO\(_2\). Sample pretreatment condition: 673K under O\(_2\) flow; 10 SCCM.](image-url)
did not show catalytic activity for the isomerization of \textit{n}-butane, although the Brønsted acid sites of SZ could be the active sites for this reaction. We found that most of the SZ calcined at 673 K was amorphous from XRD experiments. It is considered that the zirconia does not interact with sulfate species to make catalytic active sites at the calcination temperature of 673K. However, the correlations among crystal structure, acidity, and activity of SZ system have not yet been clarified, further investigation is required.

4. Conclusion
Under the supercritical conditions of \textit{n}-butane, the rapid deactivation of \textit{SO}_4^{2-}/\textit{ZrO}_2 solid was significantly retarded and a high catalytic activity was maintained. The optimum condition was 488K and 4.0MPa, which is just above the critical point of \textit{n}-butane (425K, 3.8MPa). Therefore supercritical condition is suitable for isomerization of \textit{n}-butane catalyzed by \textit{SO}_4^{2-}/\textit{ZrO}_2. It was also found that the Lewis acid sites of \textit{SO}_4^{2-}/\textit{ZrO}_2 are the active sites for the isomerization of \textit{n}-butane.

At the room temperature, SZ is hydrated as Scheme 1[a]. As the temperature is raised, the hydrated water is removed and Brønsted acid sites and Lewis acid sites are formed as Scheme 1[b]. The O-H group coordinated the Zr atoms is also removed at higher calcination temperature, and Lewis acid strength is enhanced by strong electronegativity of S=O as Scheme 1[c]. These strong Lewis acid sites contribute to the high activity on the \textit{n}-butane isomerization reaction.

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References