Isomerization of n-butane by sulfated zirconia: the effect of calcination temperature and characterization of its surface acidity

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Received 16 April 1998; accepted 15 July 1998

The distributions of Brønsted and Lewis acid sites of different acid strengths on sulfated zirconia calcined at 450–650 °C were measured by IR of adsorbed pyridine to elucidate the active sites for butane isomerization. The total numbers of Brønsted acid sites were largest when the catalyst was calcined at 500 °C. The total numbers of Lewis acid sites increased with increasing calcination temperature to a maximum at 650 °C. The catalytic activity in skeletal isomerization of butane correlated well with the number of Brønsted acid sites but not with the number of Lewis acid sites. The active sites were completely blocked by pyridine irreversibly absorbed at 350 °C. We suggest that the strong Brønsted acid sites, which are able to retain pyridine against evacuation at 350 °C, act as active sites for butane isomerization on sulfated zirconia.

Keywords: sulfated zirconia, isomerization of n-butane, Brønsted acidity, Lewis acidity

1. Introduction

Sulfated zirconia is a highly active catalyst in the isomerization, alkylation and cracking of alkanes at comparatively low temperatures [1–7]. During the early research stage, the origin of the unusually high catalytic activity of sulfated zirconia was considered to be due to strong acidity, and the catalyst was referred to as a solid superacid. This is still uncertain and under debate [7]. It has recently been claimed that the acid strength of acid sites in sulfated zirconia is lower than that of 100% H_2SO_4, ZSM-5, HX- and HY-zeolite [8–10]. Srinivasan et al. concluded that pyridinium sulfate supported on zirconia was active in the isomerization of n-hexadecane, and they claimed that Brønsted sites were not responsible for the catalytic activity [11,12]. Nascimento et al. reported that the simultaneous presence of Brønsted and Lewis acid sites was required for generation of acidity, and that the Brønsted/Lewis ratio was correlated with the catalytic activity [13], with maximum activity when this ratio was about 1. There have also been claims that the catalytic activity of sulfated zirconia derives mainly from Brønsted acid sites [14], but the effect of acidity of Brønsted sites on catalytic activity has not been discussed. Lunsford et al. reported concentrations of Brønsted and Lewis acid sites on sulfated zirconia were determined using the ^{31}P MAS NMR spectra of adsorbed trimethylphosphine. They have shown strong Brønsted acidity requires the alkylation of isobutane with 2-butene [15]. Fogash et al. and Yaluris et al. described the relationship between the acid strength distribution of the acid sites and the rate of n-butane isomerization, but it was difficult to discriminate between Brønsted and Lewis acid sites from their microcalorimetric measurements of the differential heats of ammonia adsorption used to probe the strength of the acid sites [16,17].

In the present study, the distributions of acid strength of Brønsted and Lewis acid sites on sulfated zirconias calcined at temperatures ranging from 450 to 650 °C were measured by IR of adsorbed pyridine to elucidate the active sites for n-butane isomerization.

2. Experimental

2.1. Catalyst preparation

Zirconium hydroxide was prepared by hydrolysis of zirconyl chloride ($ZrOCl_2 \cdot H_2O$, Wako Chemical, Inc.; purity >99%) with aqueous ammonia (around 25%, Wako Chemical, Inc.). Aqueous ammonia was added slowly to the aqueous solution of zirconyl chloride with vigorous stirring (600 rpm) at 50 °C, until the pH reached 3.95; then the pH was increased up to 7.90 by dropwise addition of aqueous ammonia with stirring (600 rpm). After stirring at 50 °C for 3 h, this solution was left standing for 12 h at the same temperature. The precipitated gel (zirconium hydroxide) was washed thoroughly with deionized water by decantation and filtration, dried at 110 °C for 12 h, and crushed to a diameter of less than 150 μm. The zirconium hydroxide was soaked with excess 1 N sulfuric acid solution (15 ml per g of zirconium hydroxide) with stirring for 2 h at room temperature, filtered and dried at 110 °C for

36 h. The H_2SO_4-impregnated zirconium hydroxide was heated at 1 °C/min and held at 200 °C in air for 1 h, and then calcined at 450, 500, 550, 600 or 650 °C for 3 h in air, the sample being heated to these temperatures at 1 °C/min.

2.2. Reaction procedures

The isomerization of n-butane (5.22% in N_2 balance, Takachiho Chemical Industry) to isobutane was carried out in a flow-type fixed-bed reactor at 150 °C under ambient pressure. Purity of n-butane was $>$99.4%, olefins were not detectable by gas chromatography. The content of olefins should be less than 99 ppm. The sulfated zirconia (500 mg, 355–600 μm) was pretreated at 350 °C for 20 min under a stream of He. After cooling to the reaction temperature, 150 °C, a mixture of 5.22% n-butane and N_2 balance with flowing at 10 ml/min (weight-hourly space-velocity (WHSV) of n-butane equal to 62.64 h^{-1}) was passed over the catalyst. The products were analyzed every 30 min using an on-line GC (Shimadzu GC-17A) with plot column Al_2O_3/KCl and DB-1.

For the experiments on poisoning with pyridine, the catalyst (500 mg) was pretreated at 350 °C under a vacuum for 1 h in a flow-type fixed-bed reactor, exposed to excess purified pyridine at 120 °C for 30 min, and then held at 350 °C for 30 min under a vacuum. After the poisoning treatment, the reaction was carried out at 150 °C under the same reaction conditions as described above.

2.3. Characterization

The surface area was determined by the BET method, adsorption isotherm of nitrogen at −196 °C was measured by use of a BELSORP 28SA. Prior to the adsorption measurements, all the samples were degassed at 350 °C for 20 min. The adsorption isotherms were determined over the pressure range, $P/P_0 = 0.1$–0.99. The sulfur content of the catalysts was measured by a flask-combustion method, in which the sample was combusted in oxygen and hydrogen peroxide at 1097 °C followed by determination of SO_4 content by ion chromatography.

2.4. Acid strength distribution of Brønsted and Lewis acid sites

Acid strength distribution was measured by IR spectroscopy for adsorbed pyridine used as the probe molecule to determine the Brønsted and Lewis acid sites.

Pyridine was purified by passage through 4A molecular sieves, dried and subjected to repeated freeze–pump–thaw degassing cycles. A self-supported wafer (diameter 20 mm, 40–50 mg), placed in an *in situ* IR cell with CaF_2 windows, was pretreated by outgassing at 350 °C for 1 h. The pretreated catalyst, after measurement of its FT-IR spectrum, was exposed to 1.8–2.2 Torr of pyridine at 150 °C for 30 min, and then evacuated at the same temperature for 30 min. IR spectra were measured after heating the sample stepwise at 150, 200, 250, 300 and 350 °C for 30 min under evacuation. All spectra were measured at 150 °C with an FT-IR-7000 infrared spectrometer (Japan Spectroscopic Co., Ltd.) with a DTGS detector. The FT-IR instrument was operated at a scan speed of 0.1 $cm^{-1} s^{-1}$ and with a resolution of 4 cm^{-1}, collecting 16 scans per spectrum.

Distributions of the Brønsted and Lewis acid sites on the catalyst surface were calculated from the integrated absorbances of the pyridinium ion band at 1540 cm^{-1} (due to pyridine chemisorbed on Brønsted acid sites) and the coordinately bonded pyridine band at 1440 cm^{-1} (due to pyridine chemisorbed on Lewis acid sites), respectively, employing the apparent integrated absorption coefficient of the band at 1540 cm^{-1} (3.03 cm/μmol) and that of the band at 1440 cm^{-1} (3.26 cm/μmol) [18]. The vertical unit a.u. represents the amount relative to the amount of Brønsted acid sites on which pyridine molecules are retained after evacuation at 150 °C on the catalyst calcined at 500 °C. The calculation of the number of acid sites was normalized by amount of catalyst (40–50 mg).

3. Results

3.1. Surface area and sulfur content

The properties of the catalysts prepared at different calcination temperatures are summarized in table 1. The surface areas of catalysts calcined at and below 500 °C were larger than those of catalysts calcined at and above 550 °C. The sulfur contents of catalysts were almost the same for catalysts calcined at 450–550 °C, but much lower for those calcined at 600 and 650 °C.

3.2. Catalytic activity in n-butane isomerization

The percent conversions in n-butane isomerization as a function of time on-stream are shown in figure 1 for catalysts calcined at different temperatures. Isomerization selectivities were 87–99% for all catalysts. Catalysts calcined at 550 and 500 °C showed high activities, with 12–13% conversion at the initial stage of time on-stream, but the conversion gradually decreased to less than 10% after 3 h. The catalyst calcined at 600 °C maintained 5–6% conversion, while those calcined at 450 and 650 °C showed low activities (less than 2%). The conversion value 13% corresponds to the rate value 0.101 μmol/s g-cat on the as-

Table 1
Physicochemical properties of sulfated zirconia catalysts.

Calcination temp. (°C)	Surface area (m^2/g)	Sulfur content (wt%)
450	141.5	5.8
500	149.2	6.4
550	127.6	6.5
600	104.5	2.3
650	125.5	1.4

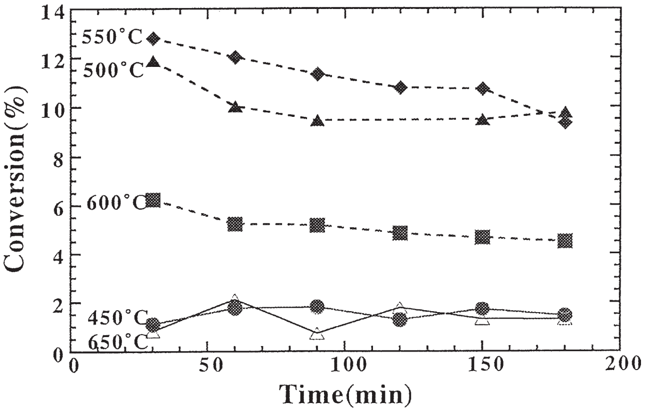


Figure 1. Effect of calcination temperature on the isomerization of n-butane.

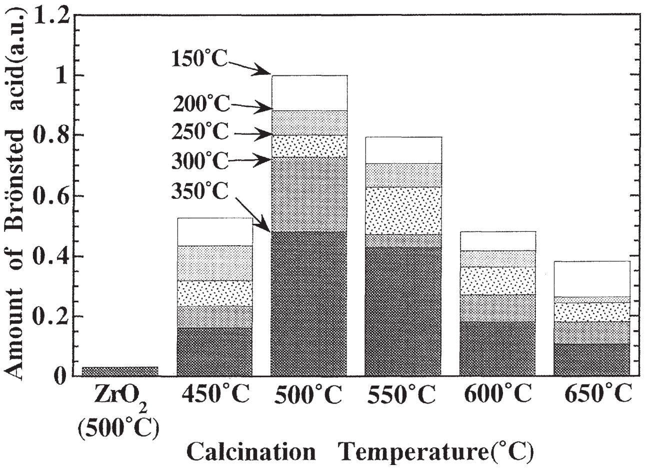


Figure 2. Brønsted acid strength distribution on sulfated zirconias and zirconium oxide.

sumption that the rate obeys first order in n-butane partial pressure.

3.3. Brønsted acid strength distribution

Acid strength distributions of Brønsted acid sites on the surface of sulfated zirconia and zirconium oxide are shown in figure 2. Each pattern shows the amounts of acid sites which desorb pyridine on increasing evacuation temperature every 50 °C. Pyridinium ions at 300 or 350 °C are defined as pyridine linked with a stronger acid site. Zirconium oxide exhibited a small number of Brønsted acid sites. In contrast, Brønsted acid sites were greatly increased by the introduction of sulfated groups. Total number of acid sites and their distribution varied with calcination temperature. Calcination at 500 °C resulted in the formation of the largest number of Brønsted acid sites. The acid sites of the catalysts calcined at 500 and 550 °C were comprised of approximately 50% of the strongest acid sites that retained pyridine against evacuation at 350 °C. The total number of Brønsted acid sites decreased with increasing calcination temperature above 500 °C. The proportion of strongest acid sites was only 30–35% for catalysts calcined at 600 and 650 °C. The number of Brønsted acid sites on the catalyst calcined at 450 °C was much lower than that on the catalyst calcined at 500 °C.

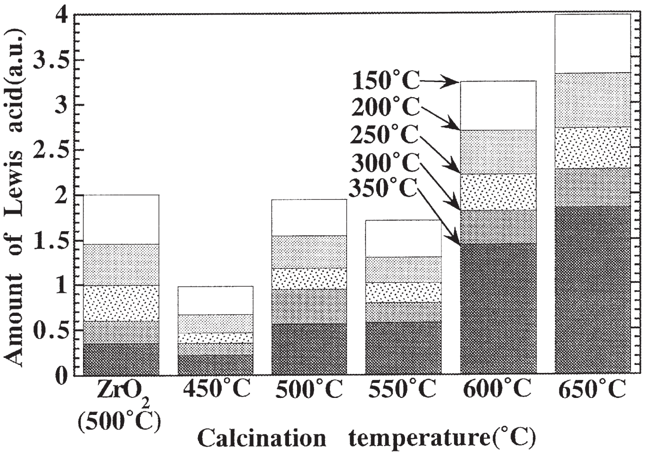


Figure 3. Lewis acid strength distribution on sulfated zirconias and zirconium oxide.

3.4. Lewis acid strength distribution

Acid strength distributions of Lewis acid sites on the surface of sulfated zirconia and zirconium oxide are shown in figure 3. Lewis acidity also depended on calcination temperature. In contrast to Brønsted acidity, which decreased with increasing calcination temperature above 500 °C, Lewis acidity continued to increase with increasing calcination temperature. The strongest Lewis acid sites markedly increased when the calcination temperature was raised from 550 to 600 °C. Note that zirconium oxide also possessed Lewis acidity comparable to that of sulfated zirconia calcined at 500 °C.

3.5. Poisoning effect of adsorbed pyridine

As shown in figure 4, isomerization did not occur over the sulfated zirconia that had been exposed to pyridine followed by evacuation at 350 °C. The sulfated zirconia was completely poisoned by pyridine which retained on the surface after evacuation at 350 °C.

4. Discussion

The number of Brønsted acid sites and their strength distribution vary with the calcination temperature. The total number of Brønsted acid sites and the strongest acid sites decreased with increasing calcination temperature except for sulfated zirconia calcined at 450 °C. Catalysts calcined at 500 and 550 °C had more Brønsted acid sites of the highest strength and showed the higher conversion. In contrast, catalysts calcined at 450, 600 and 650 °C contained lower numbers of Brønsted acid sites of the highest strength and showed lower conversion, indicating that Brønsted acid sites of the highest strength are responsible

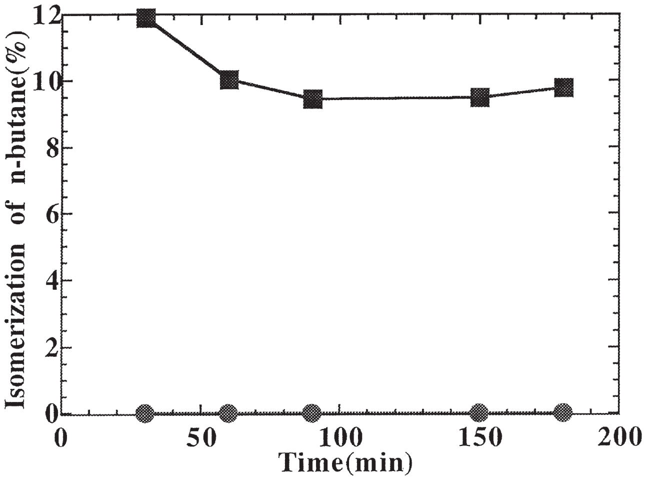


Figure 4. n-butane isomerization reaction with selective poisoning with pyridine of the highest strength acid sites on sulfated zirconia calcined at 550 °C: (■) not pyridine-adsorbed, (•) pyridine-adsorbed (sulfated zirconia had been exposed to pyridine followed by evacuation at 350 °C).

for the n-butane isomerization as active sites. The numbers of different strength Brønsted acid sites and isomerization conversion of the catalysts calcined at different temperatures are shown in figure 5 (a)–(e). The isomerization conversions were more closely correlated with the number of the highest strength Brønsted acid sites than with other acid strengths. This suggests that only the highest-strength Brønsted acid sites contribute to the n-butane isomerization reaction; conversely, acid sites of lower strength do not significantly contribute to the reaction. This is more clearly supported by the poisoning experiment with pyridine as described later.

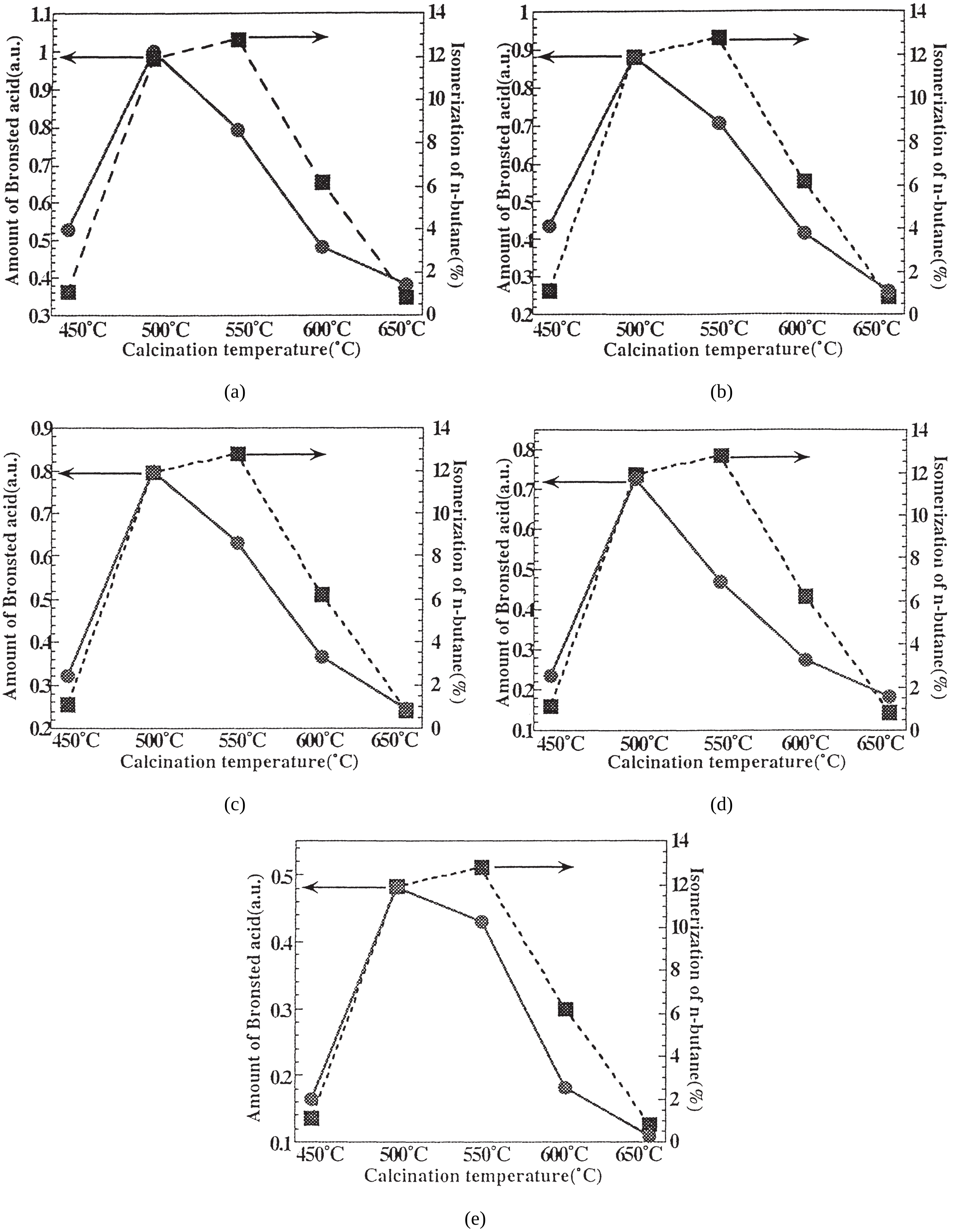
The numbers of Lewis acid sites and isomerization conversions observed for the catalysts calcined at different temperatures are shown in figure 6. Neither all nor the strongest Lewis acid sites were correlated with isomerization conversions, indicating that Lewis acid sites in sulfated zirconia are not responsible for the n-butane. This result suggests that Lewis acid sites do not contribute to the n-butane isomerization.

The catalyst was completely poisoned by pyridine adsorbed on the surface after evacuation at 350 °C for 1 h. The pyridine molecules irreversibly adsorbed at 350 °C should be adsorbed on the highest-strength acid sites. Although pyridine molecules irreversibly adsorbed on the surface are adsorbed on both Brønsted acid sites and Lewis acid sites of the highest strength, the correlation of the isomerization conversions with Brønsted acid sites of highest strength is much better than with Lewis acid sites of the highest strength. Therefore, it is strongly suggested that acid catalysts for n-butane isomerization require Brønsted acid sites of the highest strength, though it is not clear in the present study whether all or only limited numbers of the highest-strength Brønsted acid sites contribute to n-butane isomerization. Lunsford et al. suggested that strong Brønsted acid sites were needed for high catalytic activity of alkylation of isobutane with 2-butene [15]. Their result is consistent with our work on pyridine adsorption on sulfated zirconia for n-butane isomerization.

Srinivasan et al. reported that pyridinium sulfate supported on zirconia catalyzed isomerization of n-hexadecane and claimed that Brønsted sites were not responsible for the catalytic activity [12,13]. However, they did not confirm activity or the absence of Brønsted acid sites on the catalyst spectroscopically. Dumesic et al. reported the relationship between the rate of n-butane isomerization and the acid strength distribution of the acid sites which was characterized by microcalorimetric measurements of the differential heats of ammonia adsorption [16,17]. The strongest acid sites (heats from 145 to 165 kJ/mol) are responsible for the high initial activity although these sites deactivate rapidly, and the acid sites showing heats from 125 to 145 kJ/mol are less active than the former. Their microcalorimetric data could discriminate stronger acid sites, and the acid sites with heats of ammonia adsorption more than 125 kJ/mol would correspond to the acid sites with pyridine molecules irreversibly adsorbed at 350 °C.

Nascimento et al. observed that the ratio of Brønsted/Lewis ratio was correlated with catalytic activity in n-butane isomerization, with the maximum activity when the ratio was 1 [14]. However, the maximum activity at a Brønsted/Lewis ratio of unity in sulfated zirconia has no physical basis and there is no evidence of Brønsted acid sites adjacent to Lewis acid sites. The results in figures 2 and 3 indicate that the isomerization conversion rate was correlated with the number of the highest-strength Brønsted acid sites, but not with the number of the highest-strength Lewis acid sites; also, Brønsted/Lewis ratio of unity was not observed. The results in this study indicate that Lewis acid sites do not contribute to the catalytic activity.

Figure 7 illustrates the relationship between the sulfur content in sulfated zirconia and the number of Brønsted acid sites. Brønsted acidity depended on sulfur content except for sulfated zirconia calcined at 450 °C. Doping of sulfate group on zirconia greatly promoted Brønsted acidity despite the absence of Brønsted acid sites on zirconium oxide, indicating that sulfate groups strongly promote the generation of Brønsted acid sites. Some research results indicate that high sulfate loading on the zirconia creates Brønsted and Lewis acidity, resulting in high activity in dehydration of methanol and isomerization of n-butane [14,15,19,20], and that sulfate groups generate the Brønsted acid sites by promoting the acidic properties of the surface OH groups by the electron induction effect of the sulfate groups [21,22]. Sulfated zirconia calcined at 450 °C probably has more hydroxyl groups than that calcined at 500 °C, but too much hydroxyl groups in the sulfated zirconia could not serve as acid sites because the large population of hydroxyl groups would result in hydrogen bonds forming preferentially between them and allow only little interaction with neighboring sulfate groups [21]. In contrast, catalysts calcined at higher temperatures, such as 600 and 650 °C, would originally contain fewer hydroxyl and sulfate groups which results in lower Brønsted acidity.



(a) (b) (c) (d) (e)

Figure 5. Relationship between the number of different strength Brønsted acid sites in sulfated zirconia or ZrO$_2$ and isomerization conversions at different calcination temperatures: (●) number of Brønsted acid sites, (■) n-butane isomerization conversion. (a) 150 °C, (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C.

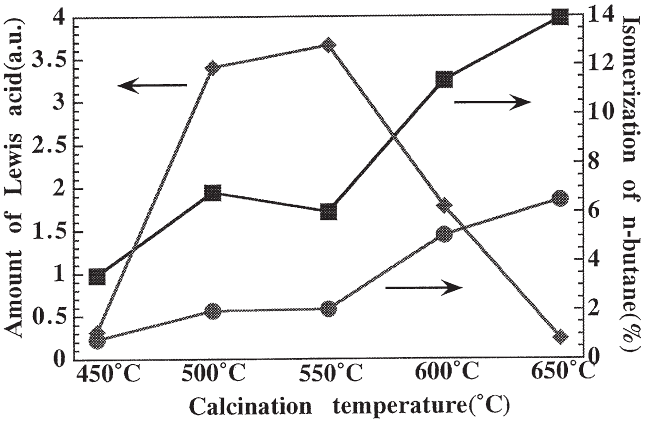


Figure 6. Relationship between Lewis acid strength in sulfated zirconia or ZrO_2 and isomerization conversion rates at different calcination temperatures: (♦) n-butane isomerization conversion rate, (■) all Lewis acid sites, (•) Lewis acid sites of the highest strength.

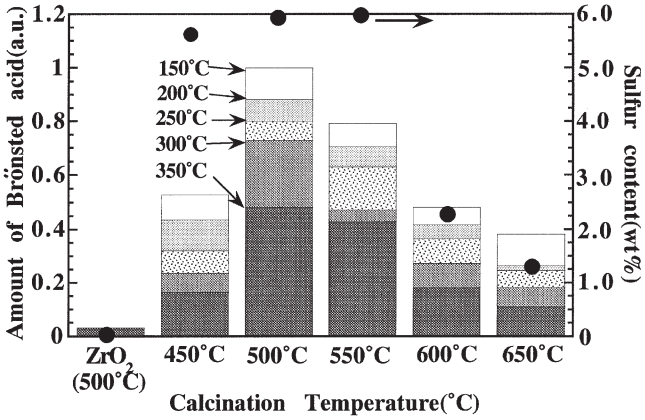


Figure 7. Relationship between the number of Brønsted acid sites in sulfated zirconia and sulfur content.

5. Conclusion

Catalytic activity of sulfated zirconia varied with calcination temperatures from 450 to 650 °C. Catalytic activity for n-butane isomerization was correlated with the number of Brønsted acid sites, particularly those sites of highest strength, although it is not clear if all or only some of the highest-strength Brønsted acid sites contribute to n-butane isomerization. Lewis acidity of the catalyst was not correlated with the isomerization conversion rate, suggesting that Lewis acid sites do not contribute to the n-butane isomerization reaction.

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