Article

The Effect of Sulfate Ion on the Isomerization of n-Butane to iso-Butane

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Abstract: The effect of sulfate ion (SO_4^{2-}) loading on the properties of Pt/SO_4^{2-}-ZrO_2 and on the catalytic isomerization of n-butane to iso-butane was studied. The catalyst was prepared by impregnation of $Zr(OH)_4$ with H_2SO_4 and platinum solution followed by calcination at 600 ℃. Ammonia TPD and FT-IR were used to confirm the distribution of acid sites and the structure of the sulfate species. Nitrogen physisorption and X-ray diffraction were used to confirm the physical structures of Pt/SO_4^{2-}-ZrO_2. XRD pattern showed that the presence of sulfate ion stabilized the metastable tetragonal phase of zirconia and hindered the transition of amorphous phase to monoclinic phase of zirconia. Ammonia TPD profiles indicated the distributions of weak and medium acid sites observed on 0.1 N and 1.0 N sulfate in the loaded catalysts. The addition of 2.0 N and 4.0 N sulfate ion generated strong acid site and decreased the weak and medium acid sites. However, the XRD results and the specific surface area of the catalysts indicated that the excessive amount of sulfate ion collapsed the structure of the catalyst. The catalysts showed high activity and stability for isomerization of n-butane to iso-butane at 200 ℃ under hydrogen atmosphere. The conversion of n-butane to iso-butane per specific surface area of the catalyst increased with the increasing amount of sulfate ion owing to the existence of the bidentate sulfate and/or polynucleic sulfate species (($ZrO)_2SO_2$), which acts as an active site for the isomerization.
Key words: sulfate ion; strong acid site; isomerization; n-butane; Zr; Pt

1. Introduction

Catalyzed isomerization of alkane is one of the important processes in petroleum refining to produce high quality gasoline because of the capability to modify the octane number of gasoline. In industrial processes, acid catalyst is known as a media for the conversion of alkane into iso-alkane. However, the catalysts such as HF, and catalysts containing halides have many disadvantages and are not suitable for the isomerization of alkanes. HF is particularly dangerous while catalysts containing halides such as $AlCl_3$ or sulphuric acid are corrosive and pose significant environmental challenges including the disposal of waste [1–3].

Considerable interest has been focused on the use of strong solid acids based on anion-modified zirconium oxide catalyst. Recently, many investigations have been focused on Pt/SO_4^{2-}-ZrO_2 because it was reported to exhibit higher activity and selectivity in the isomerization of C_4–C_6 [4,5]. In addition, the sulfated zirconia showed catalytic activities for diversified acid-catalyzed reactions at low temperature. This catalytic performance is unique when compared to typical solid acid catalysts, such as zeolites, which are mesoporous materials showing no activity for the reaction at such low temperature.

Zirconia possesses weak acid and basic properties and has no capacity for alkane isomerization. It has been realized that the catalytic activity depends on

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the acid-based properties of ZrO_2. The sulfate ion (SO_4^{2-}) content has a significant effect on the catalyst performance. The presence of SO_4^{2-} promotes the acidity and activity towards the isomerization of alkane. Yori *et al.* proposed that the addition of the SO_4^{2-} ion, an electron-rich anion, produces a very strong Lewis acid-based pair [6]. This is because of the inductive effect of the S=O groups, which produces an electronic deficiency markedly increasing the Lewis acidity of the zirconia cations.

The acid sites are classified into two groups, Broensted and Lewis acid sites. The Broensted acid site also known as the protonic acid site usually exists in the form of a hydroxyl group, whereas the Lewis acid site usually appears as an unsaturated metal. The Broensted acid site is involved in the surface intermediate formation by protonation of alkane. The protonation either to a C-H bond or to a C-C bond forms pentacoordinated carbonium ion, and this carbonium ion liberates one hydrogen or one alkane molecule while leaving the carbenium ion as intermediate in the isomerization [7].

The major concern of this research is to elucidate the effect of sulfate ion loaded on the properties of Pt/SO_4^{2-}-ZrO_2, in terms of the acidity and activity on the isomerization of *n*-butane to *iso*-butane.

2. Experimental

2.1. Preparation of catalyst

The sulfate ion-treated SO_4^{2-}-ZrO_2 was prepared by impregnation of zirconium hydroxide $Zr(OH)_4$ with H_2SO_4 aqueous solution followed by filtration and drying at 110 °C. The concentration of the H_2SO_4 aqueous solution was varied: 0.5 N, 1.0 N, 2.0 N, and 4.0 N. The SO_4^{2-}-ZrO_2 was obtained by calcination of the SO_4^{2-}-$Zr(OH)_4$ at 600 °C under static air for 3 h [8,9].

The Pt/SO_4^{2-}-ZrO_2 was prepared by impregnation of the SO_4^{2-}-ZrO_2 with $H_2Cl_6Pt\cdot6H_2O$ solution followed by drying and calcination at 600 °C in air for 3 h and obtained 0.5wt% Pt in Pt/SO_4^{2-}-ZrO_2.

2.2. Characterization of the catalyst

The surface area and the pore distribution of the catalyst were determined using a COULTER SA3100 apparatus. The sample was treated and outgassed at 300 °C for 3 h before being subjected to nitrogen (N_2) adsorption.

The X-ray powder diffraction pattern of the sample was recorded on a JEOL X-ray diffractometer JDX-3500 with a Cu-$K\alpha$ 40 kV, 45 mA radiation source. The diffraction spectrum range was 20–90° and the scanning speed and step were 1 s and 0.050°, respectively.

The ammonia TPD test was done on JEOL Multitask TPD-MS. The sample was pre-treated with He flow at 400 °C for 2 h, it was then cooled with He flow until 100 °C. The sample was outgassed at 100 °C until it reached 10^{-5} torr; the sample was then exposed to dehydrated ammonia at 100 °C for 30 min (30 torr) followed by purging with He flow to remove excess ammonia. TPD was run at room temperature up to 900 °C with a heating rate of 10 °C/min.

IR measurement was done using a Perkin-Elmer Spectrum One FT-IR Spectrometer equipped with a MCT detector. A self-supported wafer placed in an *in-situ* IR cell was pre-treated at 400 °C for 3 h and outgassed at 400 °C in hydrogen flow for 3 h. The measurements were done at room temperature. The process was repeated with the samples with different SO_4^{2-} loadings.

Thermogravimetric analysis (TGA) was conducted by the TG analysis system (Perkin Elmer Pyris Diamond TG/DTA). The sample was pre-treated under N_2 flow at 300 °C for 1 h. The sample temperature was then cooled to 50 °C before the sample was heated up to a final calcination temperature of 950 °C at a heating rate of 5 °C/min under N_2 flow.

2.3. Catalyst testing

Isomerization of *n*-butane was done in an online microreactor system at 200 °C for 15 min in the presence of hydrogen (100 ml/min, atmospheric pressure) and in saturated *n*-butane. 0.4 g of catalyst sieved to 35−80 mesh was charged for each catalytic testing. The reaction products were analyzed by online gas chromatography, using VZ-7 packed column with hydrogen, nitrogen, and helium as the carrier gases.

3. Results and discussion

3.1. Physical structure

After calcinations of pure zirconia at 600 °C and above, zirconia transforms into a monoclinic phase ($2\theta=28.3°$ and 31.4°) from a tetragonal phase ($2\theta=30.2°$) of zirconia [8]. However, the addition of

metal oxide or anion such as tungsten oxide, molybdenum oxide or sulfate ion stabilizes the tetragonal phase of zirconia and suppresses the formation of the monoclinic phase of zirconia. Figure 1 shows the XRD patterns of the prepared samples with different concentration of sulfate ion loading. The results show that the tetragonal phase is a dominant structure of zirconia and the addition of sulfate ion up to 1.0 N does not considerably change the crystallinity of the catalysts. However, further addition of the sulfate ion will collapse the structure of zirconia. In the addition of 4.0 N, a new peak associated with the monoclinic phase of zirconia was observed at 31.4°.
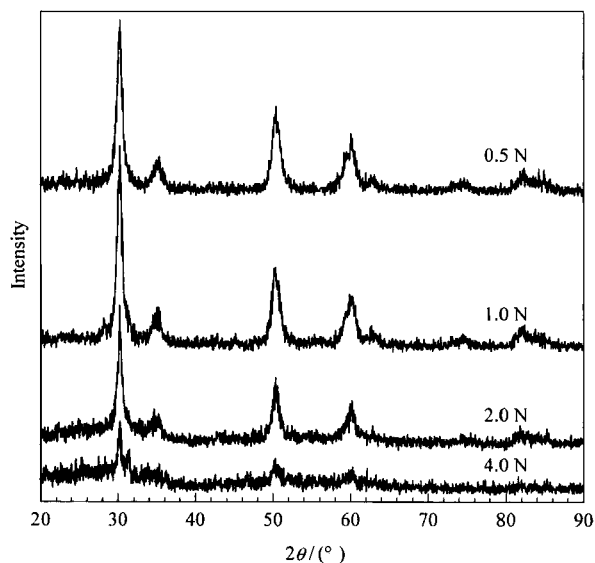

Figure 1. XRD pattern of Pt/SO_4^{2-}-ZrO_2 with 0.5 N, 1.0 N, 2.0 N and 4.0 N sulfate ion loading

Table 1 shows the specific surface area and the total pore volume for the Pt/SO_4^{2-}-ZrO_2 samples with different sulfate ion loading. The sample with 1.0 N sulfate ion catalyst obtained the largest surface area and pore volume. This catalyst has a surface area of 118 m^2/g and a pore volume of 0.127 ml/g. The addition of sulfate ion up to 4.0 N decreases the specific surface area and the total pore volume to a great extent lower than that of 1.0 N sulfate ion concomitant with the collapsing of the structure of the catalysts.

Table 1. Surface area and pore volume of the prepared Pt/SO_4^{2-}-ZrO_2 samples

Sulfate ion loading (N)	Surface area (m^2/g)	Pore volume (ml/g)
0.5	116	0.116
1.0	118	0.127
2.0	38	0.049
4.0	10	0.016

Yori *et al.* suggested that all sulfate ions are at the surface of ZrO_2 [10]. They proposed that the sulfate species form at low coverage values (corresponding to samples with sulfate loading lower than 1.0 N sulfate ion), which correspond to isolated surface SO_4^{2-} groups located in the crystallographic defective configuration (side terminations).

Sulfate species are formed up to the coverage values (corresponding to samples with 1.0 N sulfate ion), which correspond roughly to the completion of a monolayer. These species are located on the patches of low index crystal planes (top terminations of the scale-like particles); these produce Lewis and some Broensted acid sites.

When the sulfate concentration becomes higher than an average monolayer, polynucleic surface sulfates appear, probably of the pyrosulfates ($S_2O_7^{2-}$) type, which are also mainly located on the regular patches of low-index crystal planes (top terminations), and originate from Broensted sites. This circumstance leads to a reduction of the surface area and the pore volume for these samples.

Zalewski *et al.* reported that the most active catalyst system for isomerization was obtained when the sulfate loading levels approached monolayer coverage [11]. This corresponds to a surface coverage of one sulphur atom for every two zirconium atoms. The Broensted acidity also maximizes at this level. The concentration of Broensted acid sites increases as the sulfate concentration approaches monolayer coverage.

The abrupt decrease in the specific surface area for the higher sulfate species contents observed in Table 1 also correlates with the alteration of the crystal structure and the sulfate migration into the bulk phase of the solid. At high sulfate ion levels, the special stabilization of the tetragonal form starts to diminish. Thus, at a sulfate loading level higher than 1.0 N, the sulfate ion monoclinic form begins to appear [2]

3.2. Structure of the sulfate ion

Figure 2 shows a peak at about 1395 cm^{-1}, which is assigned to the asymmetric S=O stretching mode of the sulfate groups bound by bridging oxygen atoms to the surface. The S=O acts as an active acid site where this species generating stronger acid sites [12].

With increasing sulfate ion content, the band at 1395 cm^{-1} vanishes and shifts to a lower frequency, which is because of the change in the type of the sulfate species. Isolated structure of sulfate species

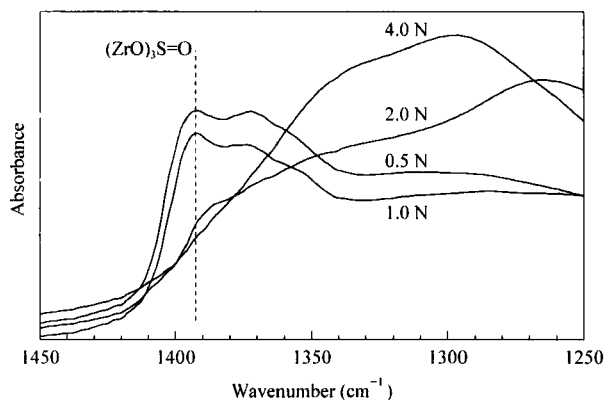$((ZrO)_3S=O)$ may change to the bidentate and/or polynucleic structure of sulfate species $((ZrO)_2SO_2)$ [13].

Figure 2. IR spectra of the sulfur species stretching region on Pt/SO_4^{2-}-ZrO_2 with 0.5 N, 1.0 N, 2.0 N and 4.0 N sulfate ion loading

3.3. Acid properties

Figure 3 shows ammonia TPD plots for Pt/SO_4^{2-}-ZrO_2 with different amounts of sulfate ion loaded. At low temperature, the TPD plots consisted of two peaks of ammonia adsorptions; the first peak at about 200 °C can be attributed to ammonia adsorbed over the weak acid site, while the second peak at about 400 °C can be attributed to the adsorption of ammonia over the medium acid site. Pt/SO_4^{2-}-ZrO_2 with 0.5 N sulfate ion obtained the highest intensity for weak acid site followed by 1.0 N, 2.0 N, and 4.0 N sulfate ions. The increase in the amount of sulfate ion decreases the intensity of the weak acid site and develops a new peak at about 400 °C for 1.0 N and new peaks at about 700−750 °C for 2.0 N and 4.0 N sulfate ions.
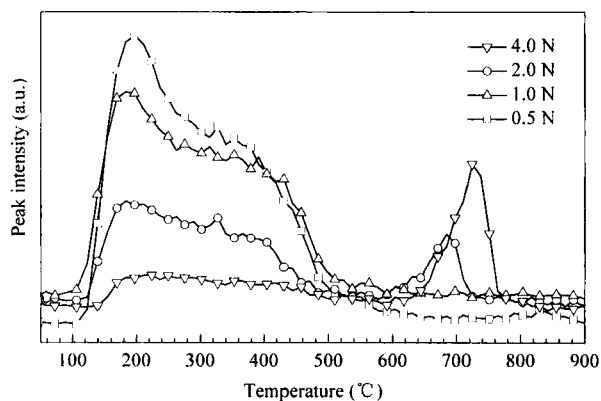
At high temperature, the peak appearing at about 700−750 °C is because of the adsorption of ammonia on strong acid site. In this region, the catalyst with 4.0 N sulfate ion obtained the highest amount adsorbed followed by the catalyst with 2.0 N sulfate ion. No-ammonia adsorption for catalysts with 0.5 N and 1.0 N sulfate ions was observed at high temperature. This phenomenon can be explained that the excessive amount of sulfate ion converted the weak and medium acid sites to strong acid sites.

The phenomena of the decrease of weak and medium acid sites and the generation of strong acid site were also strongly evidenced by the results of IR study. The spectral regions of interest on sulfated zirconia are the hydroxyl stretching regions (3000−3800 cm^{-1}). Figure 4 shows the appearance of terminal O−H on zirconia (Zr−OH) and S−OH in the catalyst. The addition of sulfate ion generates the hydroxyl groups at 3757 cm^{-1} (Zr−OH) and 3652 cm^{-1} (tri-bridged OH); further addition of sulfate ion causes eroding of the Zr−OH and the tri-bridged OH groups and develops new peaks assigned to the OH group bonded to the sulfate species (S−OH) at 3585 and 3548 cm^{-1}. This phenomenon occurs because the surface was covered by sulfate ion [12].

The physical adsorption of water on the catalyst can be observed at about 1600 cm^{-1}. Although it is not shown in the present article, the intensity of this peak decreases by the addition of sulfate ion accompanied by the decrease of the intensity of the terminal and tri-bridged OH. This result suggests that the hydroxyl groups are Broensted acid sites.
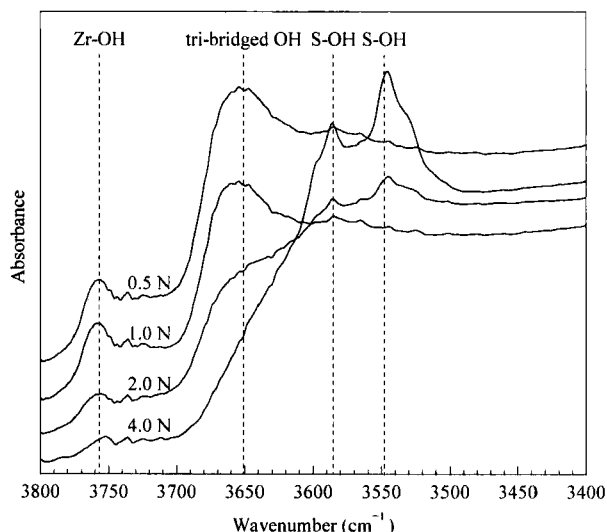

Figure 3. Ammonia TPD plot of Pt/SO_4^{2-}-ZrO_2 with 0.5 N, 1.0 N, 2.0 N and 4.0 N sulfate ion loading

Figure 4. IR spectra in the Zr−OH and S−OH stretching region on Pt/SO_4^{2-}-ZrO_2 with 0.5 N, 1.0 N, 2.0 N and 4.0 N sulfate ion loading

Although it is not shown in the present article, the TGA results explain the phenomena of weight loss, which results from heating the Pt/SO_4^{2-}-ZrO_2 sample in nitrogen flow. The curves for all samples exhibit two distinct weight loss regions. The first weight loss of about 0.15% occurs during heating up to 550 °C and this corresponds to water loss. The second weight loss at high temperature is attributed to the decomposition of the sulfate species. The percentage weight loss was about 28% for sample content 4.0 N sulfate ion. The percentage weight loss decreases with the decrease of sulfate ion loading in the sample. After being heated up to 950 °C, the percentage weight losses for samples with 0.2 N, 0.1 N, and 0.5 N sulfate ion were 16%, 6%, and 5%, respectively.

The decomposition temperature shifted towards low temperature with the increase of the sulfate ion. The decomposition temperatures for 0.5 N, 1.0 N, 2.0 N, and 4.0 N sulfate ion are 650 °C, 538 °C, 524 °C, and 517 °C, respectively. These results suggest that the sulfate ion is more strongly held on the surface at lower than at higher sulfate ion content because of the formation of the monolayer structure of the sulfate species.

It has been identified that sulfation of zirconia causes the change in the surface area and the crystalline structure of zirconia and the additional sulfate ion promotes the acidity and activity. Furthermore, it is clear that the sulfate content of the catalysts depends on the quantity of sulphuric acid used for impregnation. It is seen that the sulphur content of the catalysts increases with an increase in the quantity of sulphuric acid solution used in the impregnation.

3.4. Isomerization of n-butane

Figure 5 shows the total conversion of n-butane into *iso*-butane *per* specific surface area of the catalyst in the function of sulfate ion loading. The conversion of n-butane increases slightly with the increase of sulfate ion up to 1.0 N, and further increase of sulfate ion increases the conversion of n-butane linearly. These results reveal that the acidity of catalysts roleplay the activity of catalysts towards the isomerization of n-butane directly. The excessive amount of sulfate ion generates large number of strong acid sites, which is favourable for isomerization. It is confirmed by IR study, the shift of peaks in the range 1370–1400 cm^{-1} to a lower frequency for 2.0 N and 4.0 N sulfate ion loading catalysts may correspond to the transformation of isolated structure to the bidentate and/or

polynucleic structure of sulfate species. The bridging bidentate structure of SO_2 on the zirconia support ($(ZrO)_2SO_2$ species) causes the strong inductive effect on the Lewis acid site of Zr^{4+}, which produces an electronic deficiency markedly increasing the acidity of the zirconia cations. In the presence of hydrogen atom, the Lewis acid sites are converted to Bronsted acid sites, which are required in the isomerization of n-butane to *iso*-butane.
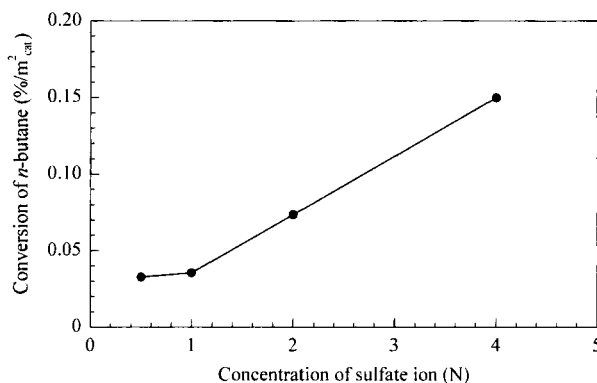

Figure 5. **Effect of sulfate ion on the conversion of n-butane**

The effects of sulfate ion loaded have been reported by several research groups. Yori *et al.* [10] and Zalewski *et al.* [11] reported that the most active catalyst system for isomerization was obtained when the sulfate loading levels approached monolayer coverage. This corresponds to a surface coverage of one sulphur atom for every two zirconium atoms. The Broensted acidity also maximizes at this level. The concentration of Broensted acid sites increased as the sulfate concentration approached monolayer coverage.

Okuhara *et al.* reported that although the strong acid and the large number of acid sites are favourable for isomerization, the cracking would be accelerated to form by-products if the acid strength is extremely high. Therefore, lowering the acid strength will result in the high selectivity [14].

4. Conclusions

This research shows that the properties of sulfated zirconia catalysts are greatly affected by the amount of sulfate ion loading. The properties, particularly the number and the strength of acid sites play an important role in the isomerization. For a limited range of sulfate loading investigated in this study of sulfated zirconia, it appears that the conversion of n-butane per specific surface area of catalysts increases with the sulfate ion loaded.

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