

The Effect of Sulfate Ion on the Synthesis of High Octane Fuel

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Abstract

The effect of sulfate ion (SO_4^{2-}) loading on the properties of $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ and catalytic isomerization of n-butane to isobutene was studied. Catalyst was prepared as follows. Zirconium hydroxide was prepared from aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ by hydrolysis with NH_4OH aqueous solution. The precipitate was filtered and washed with deionized water followed by drying to form $\text{Zr}(\text{OH})_4$. $\text{SO}_4^{2-}\text{-ZrO}_2$ was obtained by impregnation of $\text{Zr}(\text{OH})_4$ with H_2SO_4 followed by calcination at 600°C . $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ was obtained by impregnation of $\text{SO}_4^{2-}\text{-ZrO}_2$ with $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$. Pyridine adsorbed FTIR and ammonia TPD were used to confirm the acid properties of $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$. Nitrogen physisorption and X-Ray Diffractometer were used to confirm the physical structures of $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$. Sample with 1.0N sulfate ion showed a catalyst with the monolayer surface of sulfate species, existence of $(\text{ZrO})_3\text{S}=\text{O}$ (isolated structure), generation of medium acid site and presence of Brønsted and Lewis acid sites. This catalyst showed high activity and stability for isomerization of n-butane to isobutene which the reaction was carried out under hydrogen atmosphere at 200°C . However, sample with 2.0N and 4.0N sulfate ion may generate H_2S (poison) which may lead to deactivate catalyst rapidly during isomerization.

Keywords: Sulfate ion, Acid site, Isomerization of n-butane, Lewis acid, Brønsted acid

1.0 Introduction

The 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 has known as a media for conversion of alkane into iso-alkane. However, the catalysts such as HF and catalysts containing halides have many disadvantages and 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 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, studies on $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ have been focused because it was reported to exhibit higher activity and selectivity in the isomerization of $\text{C}_4\text{-C}_6$ [4,5]. In addition, the sulfated zirconia showed catalytic activities for diversified acid-catalyzed reactions at low temperature. This catalytic performance is unique compared to typical solid acid catalysts, such as zeolites and mesoporous materials, which show no activity for the reaction at such low temperatures.

Zirconia possesses weak acid and basic properties and has no capacity for alkane isomerization. It has been realized that the catalytic activity depends on the acid-based properties of ZrO_2 . The sulfate ion (SO_4^{2-}) content had 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 SO_4^{2-} ion, an electron rich-anion, produced a very strong Lewis acid-based pair [6]. This is due to the inductive effect of

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the S=O groups that 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. Broensted acid site as known as protonic acid site usually exists in form of hydroxyl group and Lewis acid site usually appears as an unsaturated metal. Broensted acid site is involved in surface intermediate formation by protonation of alkane. The protonation either to a C-H bond or C-C bond to form pentacoordinated carbonium ion, and this carbonium ion liberates one hydrogen or an alkane molecule and leaves carbenium ion as intermediates in isomerization [7].

The major concern of this research is to elucidate the effect of sulfate ion loaded on the properties of Pt/SO₄²⁻-ZrO₂, in terms of acidity and activity on the isomerization of n-butane to isobutane.

2.0 Materials and Methods

2.1 Preparation of Catalyst

The sulfate ion-treated SO₄²⁻-ZrO₂, was prepared by impregnation of zirconium hydroxide Zr(OH)₄ with H₂SO₄ aqueous solution followed by filtration and drying at 110°C. The concentration of H₂SO₄ aqueous solution was varied: 0.5N, 1.0N, 2.0N and 4.0N. The SO₄²⁻-ZrO₂ was obtained by calcination of the SO₄²⁻-Zr(OH)₄ at 600°C under static air. Catalyst will denote as XN where X is number of concentration and N is normality of sulfate ion [8,9].

The Pt/SO₄²⁻-ZrO₂ was prepared by impregnation of the SO₄²⁻-ZrO₂ with H₂Cl₆Pt.6H₂O followed by drying and calcinations at 600°C in air and obtained 0.5wt% Pt in Pt/SO₄²⁻-ZrO₂.

2.2 Characterization of Catalyst

The surface area and pore distribution of catalyst were determined using a COULTER 5A3100 apparatus. Sample was treated and outgassed at 300°C for 3 hours before subjected to nitrogen (N₂) adsorption.

X-Ray powder diffraction pattern of the sample was recorded on a JEOL X-Ray Diffractometer JDX-3500 with a Cu-K α radiation sources.

The Ammonia TPD test was carried out on JEOL Multitask TPD-MS. The sample was pretreated with He flow at 400°C for 2 hours then it was cooling with He flow until 100°C. Sample was outgassed at 100°C until reaches 10⁻⁵ torr. Then the sample was 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 to 900°C with heating rate 10°C/min.

IR measurement was carried out with 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 pretreated at 400°C for 3 hours and outgassing at 400°C in hydrogen flow for 3 hours. In the pyridine adsorption process, sample was left to contact with pyridine at 150°C for 30 minutes followed with outgassing at 400°C for 30 minutes. Measurement was done at room temperature. Process was repeated with sample with different SO₄²⁻ loading.

Termogravimetric analysis (TGA) was conducted by TG analysis system (Perkin Elmer Pyris Diamond TG/DTA). The sample was pretreated under N₂ flow at 300°C for 1 hour. Then the sample temperature was cold to 50°C before the sample was heated up to a final calcination temperature, 950°C in the heating rate 5°C/min under N₂ flow.

2.3 Catalyst Testing

Isomerization of n-butane was carried out in an online microreactor system at 200°C for 15 minutes in the presence of hydrogen and in saturated n-butane. The reaction products were analyzed using GC Shimadzu 8A equipped with VZ-7 packed column using hydrogen, nitrogen and helium as carrier gasses.

3.0 Results and Discussion

3.1 Physical Structure

Fig 1 shows the XRD patterns of prepared samples having different concentration of sulfate ion loading. In the calcination above 600°C, pure zirconia transforms into a monoclinic phase ($2\theta=28.3^\circ$ and 31.4°) from a tetragonal phase ($2\theta=30.2^\circ$) of zirconia. However, the addition of metal oxide such as sulfate ion stabilizes the tetragonal phase of zirconia. Our experimental results showed that the addition of sulfate ion up to 1.0N increased the tetragonal phase and suppressed the formation of monoclinic phase of zirconia. The further addition of sulfate ion up to 4.0N decreased both of the tetragonal phase and monoclinic phase of zirconia.

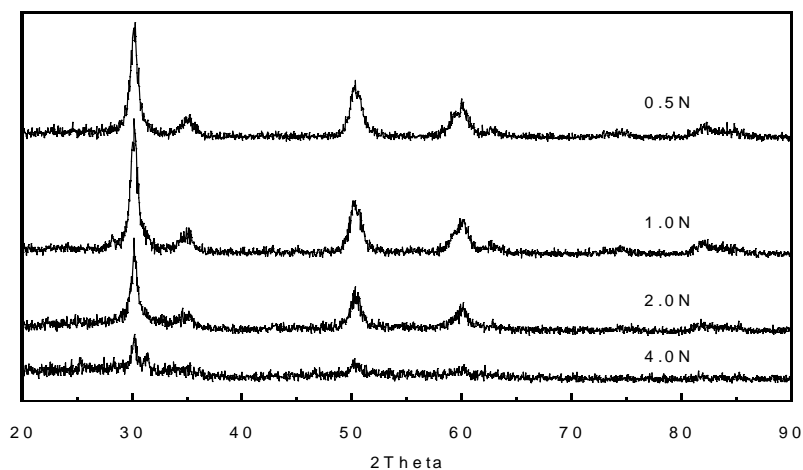


Fig. 1 XRD pattern of Pt/SO₄²⁻-ZrO₂

Figure 1 XRD patterns of prepared samples having different concentration of sulfate ion loading

Table 1 shows the surface area and pore volume for Pt/SO₄²⁻-ZrO₂ samples with different sulfate ion loading. The sample with 1.0N sulfate ion catalyst obtained the largest surface area and pore volume. This catalyst has a surface area of 118m²/g and pore volume 0.127ml/g. The surface area and pore volume decreased in increasing sulfate ion content. The surface area and pore volume for 2.0N and 4.0N sulfate ion decrease to a great extent lower than sample with 1.0N sulfate ion.

Yori *et al.* suggested that all sulfate ions are at the surface of sulfated ZrO₂ [10]. They proposed that sulfate species form at low coverage values (corresponding to samples with sulfate loading lower than 1.0N sulfate ion) which correspond to isolated surface SO₄²⁻ groups located in crystallographic defective configuration (side terminations); these species originate from Lewis acid sites.

Table 1 Surface area and pore volume of the prepared samples

Sample	Surface Area (m ² /g)	Pore Volume (ml/g)
0.5N	116	0.116
1.0N	118	0.127
2.0N	38	0.049
4.0N	10	0.016

Sulfate species formed up to coverage values (corresponding to samples with 1.0N 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); they produce Lewis and some Broensted acid sites.

When the sulfate concentration become higher than an average monolayer (corresponding to samples greater than 1.0N sulfate ion), polynuclear surface sulfates appear, probably of the pyrosulfates (S₂O₇²⁻) type which are also mainly located on the regular patches of low-index crystal planes (top terminations), and originate from Broensted site. This circumstance leads to reduction of surface area and pore volume for these samples.

Zalewski *et al.* reported that the most active catalyst system for isomerization was obtained when 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 is also maximized at this level. The concentration of Broensted acid sites increased as the sulfate concentration approached monolayer coverage.

The abrupt decreased in surface area for higher sulfate species contents observed by Table 1 correlates also with the alteration of crystal structure and 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 1.0N sulfate ion monoclinic form begin to appear [2]

3.2 Structure of Sulfate Ion

Figure 2 shows a peak at about 1395cm⁻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 act as an active acid site where this species generating stronger acid sites [12].

With increasing sulfate ion content, the band at 1395cm⁻¹ vanish and shifted to lower frequency, which is due to a change in the type of sulfate species. It may conduct due to change of (ZrO)₃S=O species, isolated structure of sulfate group to (ZrO)₂SO₂ species, polynuclear structure of sulfate group [13].

3.3 Acid Properties

Figure 3 shows ammonia TPD plots for Pt/SO₄²⁻-ZrO₂ with different amount of sulfate ion loaded. At low temperature, TPD plots consisted of two peaks of ammonia adsorptions, though they are not well separated.

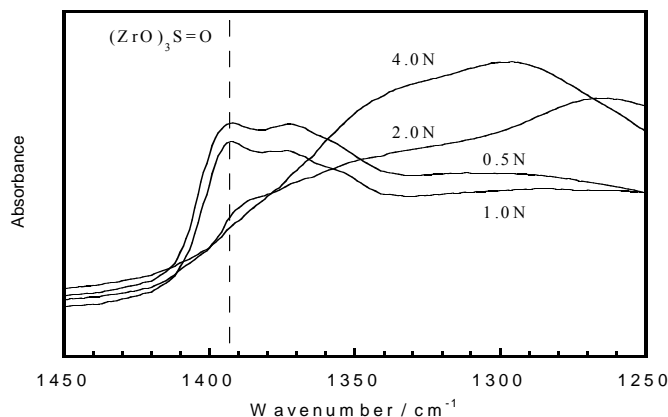


Fig. 2 IR spectra of the sulfur species stretching region

The first peak at about 200°C can be attributed to ammonia adsorb over weak acid site. While the second peak at about 400°C is due to adsorption of ammonia over medium acid site. Pt/SO₄²⁻-ZrO₂ with 1.0N sulfate ion obtained the highest intensity for weak acid site and medium acid site followed by 0.5N, 2.0N and 4.0N sulfate ion. The further addition of sulfate ion caused the reducing of the intensity of peaks assigned to weak and medium acid sites.

At high temperature, the peak appeared at about 700-750°C is due to adsorption of ammonia on strong acid site. At this region, catalyst with 4.0N sulfate ion obtained the highest amount adsorbed followed by catalyst with 2.0N sulfate ion. But, there is no ammonia adsorption for catalysts with 0.5N and 1.0N sulfate ion. This phenomenon can be interpreted that the excessive amount of sulfate ion converted weak and medium acid sites to strong acid site. Although the strong acid and the large amount of acid site are favourable for isomerization, the cracking would be accelerated to form by-products if the acid strength is too high. Therefore, lowering the acid strength would bring about the high selectivity [14].

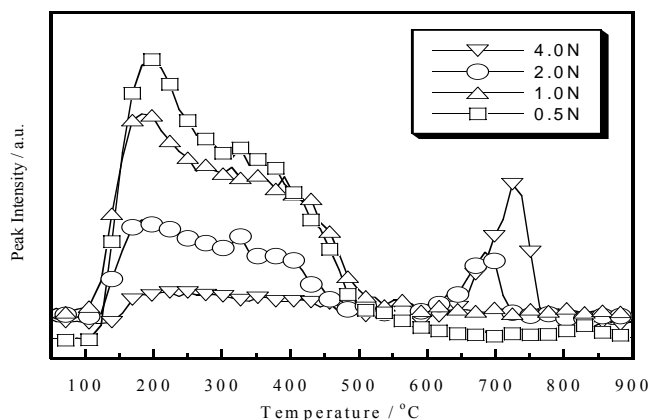


Fig. 3 Ammonia TPD plot of Pt/SO₄²⁻-ZrO₂ catalysts

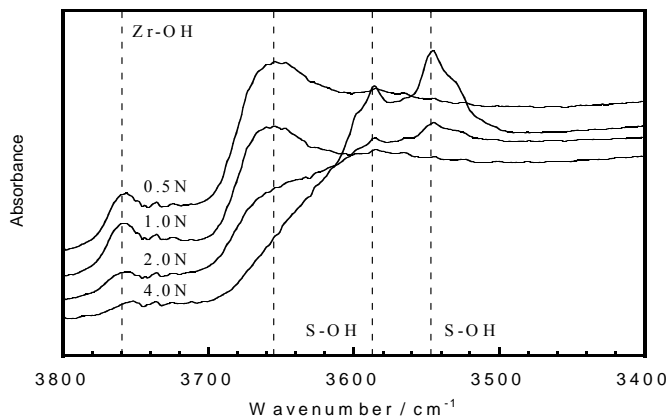


Fig. 4 IR spectra in Zr-OH and S-OH stretching region

The phenomena of decreasing 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 region ($3000\text{--}3800\text{ cm}^{-1}$). Figure 4 shows the appearance of terminal O-H on the zirconia (Z-OH) and S-OH in the catalyst. The addition of sulfate ion generated the hydroxyl groups at 3757 cm^{-1} (Zr-OH) and 3652 cm^{-1} (tri-bridged OH). The further addition of sulfate ion led to erode the Zr-OH and tribridged OH groups and developed new peaks assigned to the OH group bonded to sulfate species (S-OH) at 3585 cm^{-1} and 3548 cm^{-1} . This phenomenon occurs because the surface was covered by sulfate ion [12].

The water content of the catalyst (H_2O) could be observed at about 1600 cm^{-1} . The intensity of this peak decrease by the addition of sulfate ion accompanied the decreasing of the intensity of terminal and tri-bridged OH. This result suggests that the hydroxyl groups are Broensted acid sites.

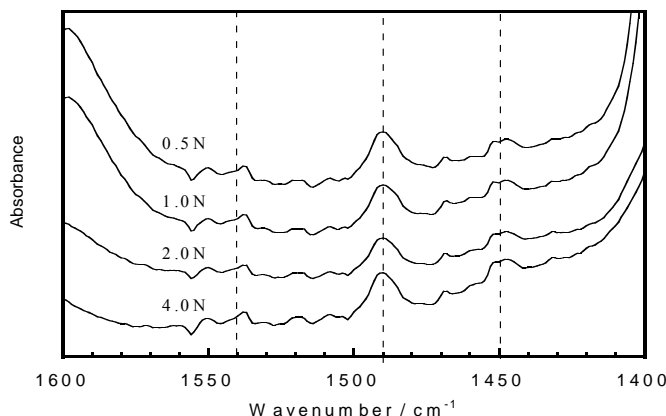


Fig. 5 IR spectra of Broensted and Lewis acid stretching region

From Figure 5, the characteristic band at 1540 cm^{-1} is assigned to pyridinium ions adsorbed on Broensted acid site. The band at 1445 cm^{-1} correspond to pyridine adsorbed on Lewis acid site and the band at 1490 cm^{-1} is due to the pyridine adsorbed on Lewis acid site and Broensted acid site. Pyridine adsorption on sulfated zirconia produced the pyridinium ion (pyridine–Broensted acid site complex), as well as covalently bound pyridine (pyridine–Lewis acid site complex).

The samples of $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ with sulfate ion content, 0.5N, 1.0N, 2.0N and 4.0N showed all

three bands, indicating both Lewis acid site and protonic acid site were present. The highest peak for both Brønsted and Lewis acid sites occurred for catalyst with 4.0N sulfate ion loaded. But for the other samples, the peak decreased in increasing of sulfate ion loaded.

The intensities for Brønsted acid site and Lewis acid site changes at the same rate for samples with 0.5N, 1.0N and 2.0N sulfate ion and this suggesting that adsorption of pyridine on Brønsted acid sites and Lewis acid sites occurred at the same rate. But for sample with 4.0N sulfate ion the intensity of adsorbed species for Lewis acid site become higher. The higher sulfate ion content causes increase in the number of strong Lewis acid sites (Stevens Jr. et al., 2003). It also reported that the position of the peak ascribed to the S=O stretching mode reflects the strength of Lewis acid sites which are associated with the sulfate group [8].

Although it is not shown in the present paper, TGA results explain the phenomena of weight loss resulting from heating the Pt/SO₄²⁻-ZrO₂ 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 sulfate species. The percentage weight loss was about 28% for sample content 4.0N sulfate ion. The percentage weight loss decreased with decreasing of sulfate ion loading in the sample. After heated up to 950°C, the percentage weight losses for sample with 0.2N, 0.1N and 0.5N sulfate ion were 16%, 6% and 5%, respectively.

The decomposition temperature shifted towards low temperature by increasing of sulfate ion. The decomposition temperatures for 0.5N, 1.0N, 2.0N and 4.0N sulfate ion are 650 °C, 538 °C, 524 °C and 517°C. These results suggested that the sulfate ion is more strongly hold on the surface at lower than at higher sulfate ion content due to formation of monolayer structure of sulfate species.

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

3.4 Isomerization of *n*-butane

Figure 6 shows the total conversion of *n*-butane into isobutene in the function of sulfate ion loading. The conversion increases in the increasing of sulfate ion up to 1.0N, however, further increasing in the amount of sulfate ion caused the decrease in the conversion of *n*-butane. The concentration of sulfate ion controls the catalytic activity until all the available surface configurations that are able to produce isolate surface SO₄²⁻ groups are occupied. From the result above, the monolayer surface SO₄²⁻ obtained by samples with 1.0N sulfate ion and it is confirmed by IR spectra according to the existence of (ZrO)₃S=O species, isolated structure of sulfate group. The S=O groups brings the inductive effect that produces an electronic deficiency markedly increasing the acidity of the zirconia cations.

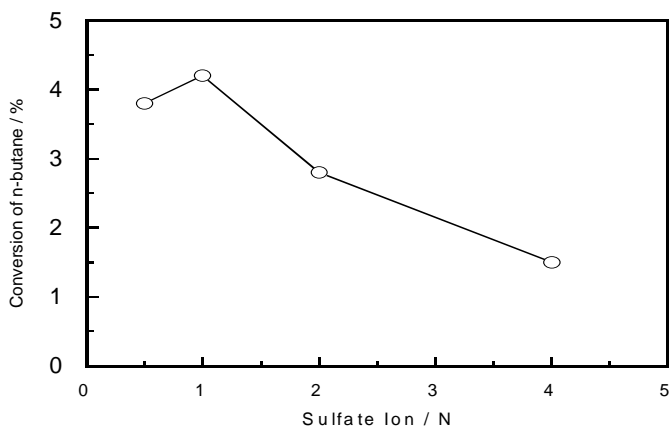


Fig. 6 Effect of sulfate ion on the conversion of n-butane.

The excess sulfate ion may increase the hydrogen uptake rate. However, the presence of platinum, hydrogen and the large amount of sulfate ion caused the evolution of H₂S and water (H₂O) which can be attributed to the reduction of sulphur oxides and poisoned the catalyst. This could occur if the strengths of the acid sites were heterogeneous and the more active ones were poisoned first. It can be seen at the sample with 2.0 and 4.0N sulfate ion which the conversion of butane decreased though the acidity increased. The sample with 1.0N sulfate ion performed high conversion because the sufficient hydrogen uptake brings to the formation of protonic acid sites and increased the catalytic activity.

4.0 Conclusion

This research showed that the properties of sulfated zirconia catalysts are greatly effected by the amount of sulfate ion loading. The properties, particularly the amount and strengthen of acid sites play an important role in the isomerization.

For the limited range of sulfate loading investigated in our study of sulfated zirconia, it appeared that the conversion of n-butane increased with the sulphate ion loaded. However, the 1.0N sulfate ion obtained the highest conversion and the presence of sulfate ion more than 2.0N will decrease the activity of catalyst.

References

- [1] Keogh, R.A., Srinivasan, R. and Davis, B.H. (1995). "Pt-SO₄²⁻-ZrO₂ Catalysts: The Impact of Water on Their Activity of Hydrocarbon Conversion." *Journal of Catalysis*. 151. 292-299.
- [2] Farcasiu, D., Li, J.Q. and Kogelbauer, A. (1997). "The Mechanism of Conversion of Hydrocarbons on Sulfated Metal Oxides. Part IV. Kinetics of the Reaction of Methylcyclopentane on Sulfated Zirconia." *Journal of Molecular Catalysis A: Chemical*. 124. 67-78.
- [3] Hara, S. and Miyayama, M. (2004). "Proton Conductivity of Superacidic Sulfated Zirconia." *Solid State Ionics*. 168. 111-116.
- [4] Ivanov, A.V., Vasina, T.V., Masloboishchikova, O.V., Khelkovskaya-Sergeeva, E.G., Kustov, L.M. and Houzvicka, J.I. (2001). "Isomerization of n-alkanes On Pt/WO₃-SO₄/ZrO₂ Systems." *Catalysis today*. 73. 95-103.
- [5] Song, X. and Sayari, A. (1996). "Sulfated Zirconia-Based Strong Solid-Acid Catalysts: Recent Progress." *Catalyst Review Science Engineering*. 38(3). 329-412
- [6] Yori, J.C and Parera, J.M. (1996). "n-Butane Isomerization on Metal-Promoted Sulfated Zirconia." *Applied Catalysis A: General*. 147. 145-157.
- [7] Olah, G.A., DeMember, J.R., and Shen, J. (1973). *Journal American Chemical Society*. 95. 4952.

- [8] Triwahyono, S. (2002). "Molecular Hydrogen-Originated Protonic Acid Sites on Zirconia-Based Catalysts." Division of Molecular Chemistry Graduate School of Engineering Hokkaido University.
- [9] Triwahyono, S., Hattori, H. and Yamada, T. (2003). "Participation of the Protonic Acid Sites Originating From Molecular Hydrogen in Alkane Skeletal Isomerization Catalyzed By Pt/WO₃-ZrO₂," *Proceeding of 13th Saudi-Japanese Catalyst Symposium Dahrhan*, Saudi Arabia.
- [10] Yori, J.C and Parera, J.M. (1995). "Preparation of Pt/SO₄²⁻-ZrO₂ by Incipient Wetness Impregnation: Influence of the Sulfur Concentration in the Isomerization of n-Butane." *Applied Catalysis A: General*. 129. L151-L156.
- [11] Zalewski, D.J., Alerasool, S. and Doolin, P.K. (1999). "Characterization of Catalytically Active Sulfated Zirconia." *Catalysis Today*. 53. 419-432.
- [12] Stevens Jr., R.W., Chuang, S.S.C and Davis, B.H. (2003). "In Situ Infrared Study of Pyridine Adsorption/Desorption Dynamics over Sulfated Zirconia and Pt-Promoted Sulfated Zirconia." *Applied Catalysis A: General*. 252. 57-74.
- [13] Tran, M., Gnep, N.S., Szabo, G. and Guisnet, M. (1998). "Influence of the Calcination Temperature on the Acidic and Catalytic Properties of Sulfated Zirconia." *Applied Catalysis A: General*. 171. 207-217.
- [14] Miyaji, A., Echizen, T., Li, L., Suzuki, T., Yoshinaga, Y. and Okuhara, T. (2002). "Selectivity and Mechanism for Skeletal Isomerization of Alkanes over Typical Solid Acids and Their Pt-Promoted Catalysts." *Catalysis Today*. 74. 291-297.