Effect of Sulfation Using Sulfate Salt Impregnation Method on Acidity of Cobalt Oxide

Hiromi MATSUHASHI *, Hiroshi TANIGUCHI, Misako HIRAI, Keita YAMAMOTO, and Junpei SUZUKI

Dept. of Science, Hokkaido University of Education, 1-2 Hachiman-cho, Hakodate, Hokkaido 040-8567, JAPAN

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To enhance the acidity of cobalt oxide, sulfation was carried out using aqueous solution of cobalt sulfate impregnated on cobalt oxide and the product calcined at high temperatures. Conventional sulfation of oxides by sulfuric acid could not avoid dissolution of cobalt oxide in the sulfuric acid. The activity of cobalt oxide for acid-catalyzed ethanol dehydration reaction was greatly enhanced by sulfation using cobalt sulfate. The activity of the prepared sulfated cobalt oxide was comparable to that of conventional SiO₂-Al₂O₃ acid catalyst. The sulfated cobalt oxide did not show activity for pentane isomerization, which was catalyzed by sulfated zirconia prepared by the same methodology of sulfate salt impregnation, using zirconium sulfate solution was impregnated onto zirconia. The highest activity was obtained by heat treatment at 1073 K. This treatment temperature is the highest among solid acid catalysts reported so far.

Keywords
Sulfation, Cobalt oxide, Acidity, Sulfate salt impregnation

1. Introduction

Cobalt is one of the important components in hydrodesulfurization catalysts. The acidity of the support for the active elements is important to increase hydrodesulfurization activity¹,², but few studies have investigated the acid properties of simple cobalt oxides³,⁴. In contrast, Co ions have been incorporated into many sulfated zirconia and sulfated iron oxides⁵ to increase catalytic activity as a promoter.

The acidity of metal oxides can be increased by the addition of sulfate ion to an oxide surface followed by heat treatment at elevated temperatures⁶,⁷. The acid strength of the metal oxides was greatly increased by such sulfation. A representative example is sulfation of iron oxide, which resulted in a large increase in acidity. Several chemical properties of iron oxide resemble those of cobalt oxide. For example, CoO and Fe₂O₃ are the more stable states of each oxide. Therefore, the acidity of cobalt oxide may be increased by introducing sulfate ions on the oxide surface and heat treatment at a higher temperature. CoO has a promotion effect on sulfated iron oxide⁸.

This study investigated the preparation of sulfated cobalt oxide and the increase in surface acidity. In general, sulfation of zirconia is performed by soaking the metal oxide in dilute sulfuric acid in the equilibrium adsorption method. However, cobalt oxide dissolves in acidic water solution. Therefore, the equilibrium adsorption method cannot be applied to introduce sulfate ions onto the cobalt oxide surface. In this study, sulfate ions were introduced onto the cobalt oxide surface by impregnation of cobalt sulfate⁹,¹⁰. To evaluate the effectiveness of the sulfate salt impregnation method, four types of zirconium oxides were sulfated by the impregnation method. Catalytic activities of the prepared catalysts for pentane isomerization and ethanol dehydration were compared. The order of catalytic activities for several acid-catalyzed reactions and the properties of zirconia gels are known¹¹. The effectiveness of the sulfate salt impregnation method was confirmed by comparing the order of activities in prepared sulfated zirconia samples with reported activities. The ethanol dehydration activity of prepared sulfated cobalt oxide was compared with that of proton-type zeolites and SiO₂-Al₂O₃ to estimate its acidity.

2. Experimental

2.1. Catalyst Preparation

The cobalt oxide gel used as a precursor of the sulfated cobalt oxide was prepared by the following method. One hundred grams of Co(NO₃)₂·6H₂O were dissolved in 2 dm³ of distilled water, followed by the addition of 0.5 mol dm⁻³ Na₂CO₃ dropwise with stirring. The precipitated product was washed seven times with 1 dm³ of distilled water, filtered with suction, and then dried at
The catalysts were prepared by the kneading method as follows. The dried cobalt oxide was mixed with (NH₄)₂SO₄ powder in a weight ratio of Co₂O₃ : (NH₄)₂SO₄ = 1 : 0.2, and ground for 30 min without solvent. The product was dried at 373 K for 24 h and then heat treated at 773-1273 K for 3 h in air. The prepared samples were kept in a sealed ampoule until use.

The sulfated cobalt oxides were also obtained by adding an aqueous solution of cobalt sulfate to cobalt oxide gel. Cobalt sulfate solution was obtained by dissolving cobalt oxide gel prepared by adding 25 % NH₄OH, followed by filtration and drying at 373 K. The prepared cobalt oxide was dissolved in water by adding the required amount of sulfuric acid. The cobalt oxide gels were soaked in the obtained cobalt sulfate solution followed by evaporation of the water, drying, and calcining in air at the desired temperature for 3 h (impregnation method). The concentration of sulfate ion was 5 wt% based on the total weight of soaked gel and cobalt oxide formed from cobalt ion in the solution. The heat-treatment temperature was varied in the range 973-1273 K. The prepared samples were kept in a sealed ampoule until use.

To confirm the effectiveness of the sulfate salt impregnation method for obtaining sulfated metal oxide, this method was applied to prepare sulfated zirconias. Four types of zirconia supplied by the Reference Catalyst Division of the Catalysis Society of Japan are available: JRC-ZRO-2, JRC-ZRO-3, JRC-ZRO-4, and JRC-ZRO-5. JRC-ZRO-2 and JRC-ZRO-5 are amorphous zirconia, usually referred to as zirconium hydroxide. JRC-ZRO-3 and JRC-ZRO-4 are crystalline zirconia, tetragonal and monoclinic, respectively, obtained by heating JRC-ZRO-2 at different temperatures. The sulfation of zirconia gel was carried out in a similar manner to that described above. Zirconium sulfate tetrahydrate was purchased from Stem Chemicals. Zirconia samples were heat treated at 923 K for 3 h.

### 2.2 Thermogravimetric (TG) and X-ray Diffraction (XRD) Analysis

To determine the amount of sulfate on the oxide surface, thermal analysis was carried out using a Rigaku TG 8120 model. Samples were heated from room temperature to 1273 K at a heating rate of 10 K min⁻¹. The content of SO₄²⁻ as SO₃ was determined from the results of the TG analysis. The weight decrease caused by the decomposition of sulfate ions was continuously observed up to 1273 K. The desorbed molecule in this stage was assumed to be SO₃, and the sulfur content was calculated based on the weight change between 773 K and 1273 K. The weight change in the higher temperature range included desorption of oxygen. The conversion of Co₂O₃ to CoO was confirmed by XRD analysis. The weight loss by reduction was subtracted from the overall weight change.

The structure of the cobalt oxides was determined by XRD analysis. The measurement was performed using a Rigaku model employing CuKα radiation.

### 2.3 Test Reactions

Ethanol dehydration into ethylene and diethyl ether, and skeletal isomerization of pentane were used as test reactions. Several limited solid catalysts can convert pentane into isopentane and isobutane. This reaction is catalyzed by strong acid sites, so the reaction is suitable to evaluate superacidity. In contrast, ethanol dehydration occurs over many acid and base catalysts. Formation of ethylene and ether is observed even on a weak acid catalyst. This reaction can evaluate acidity which is inadequate for skeletal isomerization.

Ethanol dehydration was carried out on prepared catalysts in a fixed-bed flow reactor. Heat-treated catalyst (50 mg) was placed in a glass tube and pretreated at 523 K for 2 h in a He flow of 20 mL min⁻¹. The ethanol was supplied to the reactor by passing He (20 mL min⁻¹) through an ethanol trap cooled at 273 K. The saturated vapor pressure of ethanol at 273 K is 1.5 kPa. The product was analyzed by gas chromatography, using a PEG-20 M column. Proton-type zeolites, JRC-Z5-90H (ZSM-5), JRC-Z-HB150 (beta) and JRC-SAH-1 (SiO₂·Al₂O₃) supplied by the Reference Catalyst Division of the Catalysis Society of Japan were used in this reaction to compare the catalytic activity with the prepared sulfated cobalt oxides.

Skeletal isomerization of pentane was performed in a fixed-bed flow reactor. The prepared sulfated zirconia (150 mg) was packed into a reactor made of Pyrex glass. The catalyst was heated at 573 K in a He flow (15 mL min⁻¹) for 3 h prior to the reaction. The pentane was supplied to the reactor by passing He (15 mL min⁻¹) through a pentane trap cooled at 273 K. The partial pressure of pentane in the He flow was 24.4 kPa. The reaction temperature was 303 K. The product was analyzed by gas chromatography using a TC-1 capillary column.

### 3. Results and Discussion

### 3.1 Sulfation of Zirconia by the Sulfate Salt Impregnation Method

Alkane isomerization is catalyzed by strong acid sites, including those on several solid catalysts, such as mordenite, ZSM-5, beta zeolite, and heteropolyacids, as well as catalysts of the sulfated zirconia family. Polymerization of surface alkenes occurs, and the polymer product is converted into a carbon deposit acting as a catalyst poison in a bimolecular reaction. The accumulation of carbon deposits on the catalyst surface causes a rapid decrease in the catalytic isomerization activity.

The time course of the pentane isomerization activity...
of sulfated JRC-ZRO-5 prepared by the impregnation method is shown in Fig. 1. The observed products were isopentane and isobutane, as well as a small amount of hexane isomers. The vertical scale of Fig. 1 is the carbon percentage of products among the total hydrocarbons detected. An induction period was observed for the catalytic activity and the product composition. The pentane isomerization activity increased in the initial stage and isobutane formation occurred after this increase in activity. After the activity peaked, the catalyst was deactivated quickly and formation of isobutane stopped. The isopentane was the only product in the induction period. Later, increased activity was observed together with the formation of isobutane. Isobutane is known to be formed if the reaction proceeds by the bimolecular mechanism after the induction period. The product composition indicates that the monomolecular reaction is predominant in the induction period, then the bimolecular mechanism predominates with the increase in reaction rate. The intermediate for the bimolecular reaction accumulates in the induction period, so the increase in the reaction rate is observed following the buildup of the intermediate. The buildup of the intermediate for the bimolecular reaction also causes catalyst poisoning. Therefore, excess accumulation of intermediates results in deactivation of the bimolecular reaction. After such rapid deactivation, isomerization occurs through the monomolecular mechanism.

The isomerization activities of the catalysts in the initial stage and at the peak are summarized in Table 1. The activity in the initial stage depends on the simple proton abstraction ability of the Lewis acid sites. The order of pentane isomerization activity of the sulfated catalysts in the initial stage was $5 > 2 > 3 > 4$. This order is the same as that of zirconia catalysts sulfated by a conventional method using dilute sulfuric acid. The effect of sulfation is higher over amorphous zirconia. Catalysts prepared by zirconium sulfate impregnation showed activity for pentane isomerization. The effect of the starting zirconia gel on the catalytic activity for acid-catalyzed skeletal isomerization of alkane was the same as that observed on catalysts prepared by the equilibrium adsorption method. Therefore, the zirconium sulfate impregnation method can be used to prepare sulfated metal oxide catalysts.

The sulfate salt impregnation method was applied to prepare sulfated cobalt oxide. However, the prepared sulfated cobalt oxides did not show any activity for pentane isomerization at this low reaction temperature.

### 3.2. Dehydration of Ethanol over Sulfated Cobalt Oxide

The results of ethanol conversion over cobalt oxide and sulfated cobalt oxide catalysts, proton-type zeolites (ZSM-5, beta), and $\text{SiO}_2 - \text{Al}_2\text{O}_3$ are illustrated in Fig. 2. The horizontal axis is the reaction temperature and the vertical axis is the conversion of ethanol. The dehydration products were ethylene and diethyl ether. The conversion is the ratio of the amounts of ethylene and diethyl ether products to the total amount of compounds detected. All data of sulfated cobalt oxides heat treated at various temperatures are plotted at the reaction temperature of 453 K. Ethanol conversion was observed in the range from 3.7 to 7.7% in the case of sulfated samples. The activity depended on the heat treatment temperature and preparation method.

![Fig. 1](image)

**Table 1** Pentane Isomerization over Sulfated Zirconia Catalysts Prepared by Zirconium Sulfate Impregnation

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Initial</th>
<th>Highest</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conversion [%]</td>
<td>Isopentane selectivity [%]</td>
</tr>
<tr>
<td>ZRO-2</td>
<td>0.9</td>
<td>100</td>
</tr>
<tr>
<td>ZRO-3</td>
<td>0.7</td>
<td>100</td>
</tr>
<tr>
<td>ZRO-4</td>
<td>0.2</td>
<td>100</td>
</tr>
<tr>
<td>ZRO-5</td>
<td>1.8</td>
<td>100</td>
</tr>
</tbody>
</table>

Catalyst amount: 150 mg, He flow: 15 mL min$^{-1}$, pentane pressure: 24.4 kPa, reaction temperature: 303 K.

○: Total conversion, □: isopentane, ◐: isobutane.
This observation will be discussed later. Untreated cobalt oxide showed lower activity. The reaction temperature had to be increased by more than 120 K to obtain a similar conversion of ethanol over untreated cobalt oxides. The catalytic activity of the solid acid was enhanced by sulfation by cobalt sulfate impregnation or kneading with ammonium sulfate, followed by heat treatment at higher temperatures.

The dehydration activity of sulfated cobalt oxides was lower than that of ZSM-5 and beta. These two zeolites and mordenite have adequate acidity for skeletal isomerization of alkanes at elevated temperatures\(^{18}\). The lower activity of sulfated cobalt oxides indicates that the acid strength of the prepared solid acids was insufficient for skeletal isomerization. The activities of sulfated cobalt oxides were comparable with that of SiO\(_2\)-Al\(_2\)O\(_3\), a representative solid acid. SiO\(_2\)-Al\(_2\)O\(_3\) has no activity for skeletal isomerization, as cracking of alkanes is predominant at elevated temperatures.

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The effect of heat-treatment temperature on the dehydration activity is shown in Fig. 3. The highest activity for ethanol dehydration was given by activation at 1073 K with the sample sulfated by the kneading method. This activation temperature is much higher than those reported for sulfated metal oxides. Among the reported sulfated metal oxides, sulfated hafnium oxide has the highest activation temperature at 973 K\(^{10}\). In many cases of sulfated metal oxides, the acidity disappears after heat-treatment at higher temperatures due to the decomposition of surface sulfate groups. This result indicates that the sulfate ions on the cobalt oxide surface were the most stable among the reported sulfated metal oxides.

The comparison of methods of sulfate ion introduction showed that catalysts prepared by the cobalt sulfate impregnation method had slightly higher activity than those prepared by the ammonium sulfate kneading method. The highest activity was obtained by heat treatment at 973 K of cobalt sulfate impregnation samples (8.8 % conversion), and at 1073 K of kneading samples (6.4 %). The sulfated catalysts prepared by both methods had the same catalytic activity as that obtained with high-temperature treatment at 1173 K.

3.3 TG and XRD Analyses

TG and XRD analyses were performed to determine the active crystalline structure of the untreated and sulfated cobalt oxide samples. The results of the TG analysis are shown in Fig. 4. Steep decreases in weight were observed around 500 K and 1200 K for untreated cobalt oxide. The crystalline structures of cobalt oxides heat treated at 773 K and 1273 K were CoO\(_4\) and CoO, respectively. The steep decrease in weight at 1200 K was due to desorption of O\(_2\) accompanied by conversion of CoO\(_4\) to CoO.

TG curves of sulfated cobalt oxide samples prepared by the impregnation method and the kneading method are also shown in Fig. 4. The large decrease in weight observed in the range from 500 to 700 K for the impregnation sample was due to the dehydration of cobalt oxide gel. The temperature range of the dehydration...
process was increased by the impregnation treatment. The crystalline structure of sulfated cobalt oxide was determined as Co$_3$O$_4$ by XRD analysis. The weight of the impregnation sample gradually decreased after dehydration. The structure of the sulfated cobalt oxide also gradually changed to CoO from Co$_3$O$_4$. The sample heat treated at 973 K was Co$_3$O$_4$. After heating at 1173 K, the sample mainly consisted of Co$_3$O$_4$, and a small peak set of CoO was observed, as shown in Fig. 5. The crystalline structure changed completely to CoO after heating at 1273 K. However, the rapid decrease in weight was eliminated by impregnation of cobalt sulfate. This observation is very similar to the disappearance of the exothermic peak accompanied by phase change from tetragonal to monoclinic induced by sulfation of zirconium oxide$^{21)}$.

No weight loss in the higher temperature range was observed for both the sample sulfated by the kneading method and by the impregnation method. The CoO peak set was found for the sample heat treated at 1173 K, as shown in Fig. 6, but was converted completely into CoO by heat treatment at 1273 K. However, no rapid weight loss was observed. Strong inhibition of crystallization by sulfation is commonly found in the solid superacids of sulfated metal oxides$^{12,21)}$. Sulfate ions are reported to lower the reducibility of Co(III)$^{22)}$.

The relationship between the heat-treatment temperature of catalysts and the amount of sulfate as SO$_3$ is shown in Fig. 7. The gradual weight decrease observed in the higher temperature range in the TG profile was due to surface sulfate decomposition and conversion of Co$_3$O$_4$ to CoO. The weight of Co$_3$O$_4$ was calculated assuming that the remaining material was pure CoO. The remaining weight, which involved subtracting that of O$_2$ calculated from lost weight in the temperature range from 773 to 1273 K, was converted into the weight of SO$_3$ decomposed$^{15)}$. The effect of heat-treatment temperature on the content of SO$_3$ was small on sulfated cobalt samples prepared by the impregnation treatment.
impregnation method. The effectiveness of this preparation method was confirmed by the results of sulfated zirconia preparation compared with catalysts prepared by the conventional method. The sulfated cobalt oxide catalysts were also prepared by the ammonium sulfate kneading method. The activity for acid-catalyzed reaction of ethanol dehydration was greatly enhanced by sulfation. Crystallization and conversion into CoO from Co₃O₄ were strongly inhibited by sulfation. The activity of ethanol dehydration depended on the amount of SO₃ when the catalyst was activated at 1073 K or higher. The highest activity was obtained for the sample prepared by the impregnation method followed by heat treatment at 973 K. The highest activity for the sulfated cobalt oxide prepared by the kneading method was obtained at 1073 K. This activation temperature is the highest among sulfated metal oxides.

4. Conclusion

To enhance the acidity of cobalt oxide catalyst, sulfated cobalt oxide was prepared with the sulfate salt impregnation method. The amount of SO₃ was greatly decreased by heat treatment at 1073 K on the sulfated cobalt oxide samples prepared by the kneading method. The catalytic activity of the kneading sample was increased in the temperature region lower than 1073 K. This result indicates that the sulfate ions decomposed at a temperature lower than 1073 K are not involved in increasing the acid strength over the cobalt oxide surface. The amount of sulfate ions on catalysts heat treated at 1273 K was the same in both preparation methods. The activities were also almost the same, as shown in Fig. 3. Catalysts with a large amount of SO₃ showed higher dehydration activity if heat treated at 1073 K or higher. The activity was strongly related to the amount of SO₃ in this heat-treatment temperature range. The remaining sulfate ions after heat treatment at the higher temperature would form strong acid sites. This result indicates that sulfate salt impregnation was effective for preparing sulfated cobalt oxide catalyst.

The sulfated cobalt oxide prepared by the cobalt sulfate impregnation method and heat treated at 973 K was applied to the skeletal isomerization of pentane. However, this catalyst had no activity for the reaction. No superacidity was generated on the cobalt oxide by sulfation.

References

要     旨

酸化コバルトの酸性度に対する硫酸塩含浸法による硫酸化の影響

松橋 博美, 谷口 央, 平井 美佐子, 山本 啓太, 鈴木 絢平

北海道教育大学, 040-8567 北海道函館市八幡町1-2

酸化コバルトの酸性度を向上させるため、酸化コバルトを硫酸化した。その際、硫酸コバルト水溶液を含浸液として用いることとし、得られた化合物を高溫で焼成した。通常の酸化物硫酸塩化の方法では硫酸を用いるが、酸化コバルトは硫酸に溶解してしまうためである。酸触媒反応であるエタノール脱水反応に対する酸化コバルトの触媒活性は、硫酸塩化により著しく向上した。本触媒の活性は、酸触媒であるシリカルミナ触媒に匹敵した。本研究で提案した方法にて調製した硫酸化ジルコニア、すなわち酸化ジルコニアをジルコニアに含浸担持して得たもので、触媒することのできるペンタン異性化には、本硫酸化酸化コバルトは活性を示さなかった。最高活性は1073 Kでの加熱で得られた。この温度はこれまでの硫酸化金属酸化物の中で最も高かった。

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