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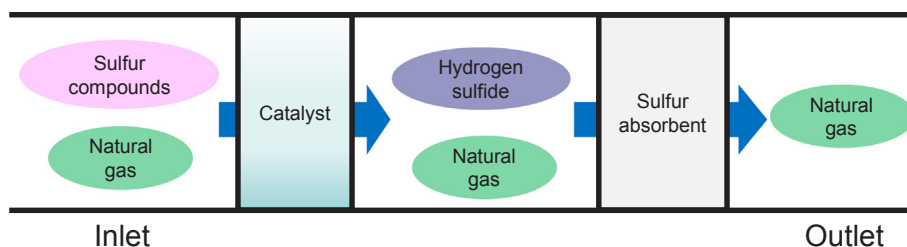
Development of oxide-supported nickel-based catalysts for catalytic decomposition of dimethyl sulfide



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GRAPHICAL ABSTRACT

Catalytic Direct-Decomposition Desulfurization Process

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ABSTRACT

We have developed a heterogeneous catalyst for the decomposition and removal of dimethyl sulfide used as an odorant in fuels such as city gas in residential fuel cell systems. For the dimethyl sulfide decomposition at 500 °C over various oxides such as γ -Al₂O₃, TiO₂, ZrO₂, CeO₂, SiO₂, and MgO, it was found that adsorption of dimethyl sulfide and other products containing sulfur components, sulfuration of metal oxides, and decomposition of dimethyl sulfide occurred. Namely, dimethyl sulfide could be removed from the reaction gas by several reactions. Furthermore, the loading of the nickel component on γ -Al₂O₃ as a metal component led to high decomposition performance. Based on the XRD, H₂-TPR, and UV-Vis spectra analyses, after the preparation, this catalyst exists in the state of nickel oxide and nickel aluminate supported on γ -Al₂O₃. However, upon exposure to the dimethyl sulfide or hydrogen sulfide feed, the sulfuration reaction of nickel species proceeds, leading to the transformation of the material to nickel sulfide and the enhancement of the decomposition reaction. Furthermore, based on the results of the optimization of the nickel loading amount, we revealed that the 10 wt% supported catalyst was the best catalyst.

1. Introduction

A fuel cell system is a cogeneration system that produces electricity and heat from oxygen and hydrogen in a highly efficient and clean power generation process [1]. Hydrogen derived from renewable energy is desired in the manufacturing process of hydrogen to be used for fuel cells in the future. However, currently, reforming of fossil fuels is a

major source of hydrogen. Natural gas, which is one of the fossil fuel resources, is inexpensive and is known to generate less CO₂ emissions during combustion than other fossil fuels. Natural gas can be classified as “Liquefied Natural Gas” (LNG) and “Pipeline Natural Gas” (PNG) based on the different of transportation systems [2]. Indeed, natural gas becomes liquid (LNG) at the concentration below the boiling point (−162 °C) of the main component methane (CH₄). In other words, it

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can be said that LNG is superior for storage and transportation because liquefaction reduces the volume to *ca.* one six hundredths of the volume of the gas state. Most of natural gas distributed in Japan is used in the form of LNG. LNG is almost pure hydrocarbon because impurities are removed during the liquefaction process and a specific sulfur compound is added as an odorant at 1–3 ppm for leakage detection. For this purpose, *tert*-butyl mercaptane (TBM, C₄H₉SH) and dimethyl sulfide (DMS, C₂H₆S) are often used. By contrast, PNG is natural gas that is transported via a pipeline directly following extraction. Therefore, unlike for LNG no purification process is required. However, thiols (such as TBM), methyl mercaptane (CH₃SH), sulfides (such as DMS), hydrogen sulfide (H₂S), carbonyl sulfide, and other wide variety of sulfur compounds are included in PNG. These sulfur components significantly deteriorate the catalytic performance by poisoning the steam reforming catalyst and the water-gas shift catalyst in the reformer in the fuel cell generation systems [3–13]. Therefore, a desulfurization process is indispensable for fuel cell systems using a fossil fuel as fuel.

In industrial plants, flue gas desulfurization technology is widely used to remove sulfur oxides (SO_x). On the other hand, a hydrodesulfurization (HDS) method and an adsorptive desulfurization (ADS) method have been proposed for the desulfurization process in a residential fuel cell system. For the currently used residential fuel cell systems, odorants such as TBM and DMS are removed by the ADS method using suitable zeolites [14–19]. In particular, Ag ion exchanged Y-type zeolite shows an excellent adsorption performance [20]. However, because TBM is more strongly adsorbed than DMS, the adsorbed DMS is eliminated by substitution with TBM, as reported by Takatsu et al. [21]. Furthermore, Kim et al. reported the adsorption properties of Cu/ZnO/Al₂O₃ using a mixed gas of DMS, TBM, and tetrahydrothiophene [22]. They also found that the adsorbed amount of DMS was the smallest and only *ca.* one third of the adsorption amount of TBM could be removed; this tendency was remarkably confirmed when the adsorption temperature was in the range of 50–350 °C. As described in their work, it is difficult to remove DMS by adsorption, and the risk of reversible desorption is greater than that of the other sulfur compounds. Therefore, we have proposed a catalytic direct-decomposition desulfurization (CDDS) process for DMS as a new desulfurization method [23].

Several studies on the conversion of DMS into other sulfur compounds over the solid catalysts have been reported so far. Koshelev et al. synthesized CH₃SH from DMS at 450–550 °C using γ -Al₂O₃ [24]. They reported that MM can be formed by reacting DMS with H₂S. Mashikin et al. and Chen et al. also studied the thiolation reaction of DMS using γ -Al₂O₃-based catalysts at the reaction temperatures in the 400–450 °C range [25,26]. They reported that the activity was improved by using the γ -Al₂O₃ modified phosphorus component. Among the catalysts other than γ -Al₂O₃, Chen et al. reported that similar reactions occurred over WO₃/ZrO₂ [27]. In addition, Ziolk et al. investigated the decomposition reaction of DMS at 450–500 °C over Y-type zeolite, and reported that ethyl mercaptane (C₂H₅SH) and hydrocarbons were formed [28,29]. They concluded that the Brønsted acid sites affect the decomposition reaction of sulfur compounds. However, there have been no reports on the reaction of direct decomposition of DMS into H₂S. In addition, the reactivity of the catalysts is quite low and the reaction is carried out at the high temperature of 500 °C even for the studies of the synthesis process of other sulfur compounds from DMS. This indicates that an activation of DMS is significantly difficult.

In our proposed CDDS method, it is assumed that DMS is decomposed into H₂S and the generated H₂S is fixed with zinc oxide (ZnO) or a similar material. Moreover, it is possible to adsorb and remove CH₃SH to some extent with ZnO. However, for use in a hydrogen production process for fuel cell systems, it is necessary to avoid the generation of sulfur compounds other than H₂S and CH₃SH as much as possible. Based on these considerations, the present research aims to develop a catalyst capable of activating DMS at a low temperature of 400 °C and of decomposing DMS into H₂S, focusing mainly on Ni-based catalysts.

2. Experimental

2.1. Catalyst preparation

The following several oxides were used in the present work. Gamma-Al₂O₃ (γ -Al₂O₃) was obtained by the calcination of the boehmite (α -Al(OOH), aluminum hydroxide) purchased from Sasol at 600 °C for 2 h. As other oxides, CeO₂ (JRC-CEO-1), SiO₂ (JRC-SIO-6), TiO₂ (JRC-TIO-8), amorphous zirconium hydroxide (JRC-ZRO-2), and MgO (JRC-MGO-4) obtained from the Catalyst Society of Japan were calcined at 500 °C for 2 h prior to use.

As a supported metal catalyst, γ -Al₂O₃ was used as a support and Ni, Co, Mo, and W components were supported by the conventional impregnation method [30,31]. A predetermined amount of γ -Al₂O₃ support was mixed with distilled water in an eggplant flask followed by the addition of a predetermined amount of each metal nitrate solution. As a starting material for each metal, nickel nitrate (II) hexahydrate (Kanto Chemical), cobalt nitrate (I) hexahydrate (Kanto Chemical), seven molybdate hexaammonium tetrahydrate (Kanto Chemical), and ammonium tungstate Pentahydrate (Kanto Chemical) were used. The metal loading amount was adjusted to 10 wt% in the metal state, unless otherwise specified. The mixture solution was stirred and evaporated to dryness under a reduced pressure in a water bath at 80 °C. The obtained powder sample was dried at 110 °C overnight and then calcined in air at 500 °C for 2 h to obtain a metal oxide supported metal catalyst. All oxides and supported metal catalysts were molded and crushed to the particle size of 150–250 μ m for use in the DMS decomposition test.

2.2. DMS decomposition test

DMS decomposition test was conducted in a fixed bed flow reactor under atmospheric pressure. 500 mg of each catalyst was set in a quartz tube (*i.d.* 6 mm) and the reaction gas mixture (10 ppm or 100 ppm DMS/N₂ balance) was fed into the catalyst bed at the total flow rate of 500 mL min⁻¹. Sulfur compound components and hydrocarbon components in the effluent gas were analyzed using a gas chromatograph equipped with a hydrogen flame photometric detector (GC-FPD, Shimadzu, GC-14BPF) and a gas chromatograph with a flame ionization detector (GC-FID, Shimadzu, GC-8AIF). To separate the gaseous products, a 1, 2, 3-TCEP 25% Shimalite 80/100 AW-DMCS-ST G-5278 column (Shinwa Chemical Industries) and a BX-10 column (GL Science) were used for GC-FPD and GC-FID, respectively. Prior to the reaction test over the supported metal-based catalysts, a sulfurization pretreatment was carried out at 500 °C in 1000 ppm H₂S/N₂ as the sulfur compound taking into consideration the treatment time so that the sulfur species can flow only in an amount sufficient to sulfurize the metal component contained in the catalyst.

2.3. Characterization

2.3.1. Nitrogen (N₂) adsorption and desorption

The physical property of each sample was evaluated using N₂ adsorption and desorption isotherms at 77 K using a MicrotracBEL BELSORP-mini II instrument. Prior to N₂ adsorption and desorption measurements, the sample was degassed at 150 °C for 2 h in order to remove the moisture adsorbed on the surface and inside the porous network. The Brunauer-Emmett-Teller (BET) method was used to estimate the specific surface area from the obtained adsorption data.

2.3.2. X-ray diffraction (XRD)

To identify the crystalline structure of each sample, the powder XRD patterns were measured using a Rigaku Ultima IV instrument equipped with a Cu K α radiation source (λ = 0.154 nm). The acceleration voltage and current were 40 kV and 40 mA, respectively, and each measurement was conducted with the scanning speed of 2.0° min⁻¹ and the step size of 0.01°.

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