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# Catalytic decomposition of methanethiol to hydrogen sulfide over $TiO_2$

Takashi Mukoyama, Naohiro Shimoda, Shigeo Satokawa *

*Department of Materials and Life Science, Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan*

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ABSTRACT

As a new desulfurization process for fuel cell systems, catalytic direct decomposition of methanethiol into hydrogen sulfide on various metal oxides without hydrogen addition has been examined. Methanethiol was decomposed into hydrogen sulfide over several metal oxide catalysts at 300 °C. Major metal oxide catalysts used in this study decomposed methanethiol completely at 500 °C. However they would be sulfurized immediately by the decomposed products. Among them, titania ($TiO_2$) catalyst exhibited a remarkable methanethiol decomposition activity and it was hardly sulfurized. The methanethiol conversion of $TiO_2$ catalyst depended on the specific surface area. Hydrogen sulfide and dimethyl sulfide were produced with the same amount at below 250 °C. The methanethiol seems to be decomposed by the following equation at low temperature range: $2CH_3SH \rightarrow H_2S + (CH_3)_2S$. In contrast, hydrogen sulfide and methane were produced as gas phase products and carbon species were also formed on $TiO_2$ surface above 400 °C. The methanethiol seems to be decomposed by the following equation at high temperature range: $2CH_3SH \rightarrow 2H_2S + CH_4 + C$. We conclude that the direct decomposition of methanethiol on $TiO_2$ surface proceeds *via* different reaction pathways depending on the reaction temperatures.

## 1. Introduction

In recent years, the development of high efficient and clean energy conversion systems has become increasingly important in order to reduce carbon dioxide emission. The stationary fuel cell co-generation system is one of the most promising candidates as a highly efficient and clean energy conversion system. The co-generation system can utilize waste heat during power generation. Installation of a decentralized fuel cell system has many advantages to reduce transmission loss and to utilize waste heat, and also has been increasingly sought with the view of securing an emergency power source. Therefore, the residential fuel cell co-generation system has been attracting much attention [1,2].

Hydrogen production for power generation by a residential fuel cell system is carried out by the steam reforming reaction process of natural gas. The sulfur compounds contained in the natural gas must be removed because they deteriorate the steam reforming catalysts [3–5]. Generally, a hydrodesulfurization (HDS) process is selected as a general industrial desulfurization technology [6–9]. The sulfur-containing compounds contained in crude oil and natural gas fuels can be removed by the catalytic HDS process which is operated at elevated temperatures (300–450 °C) with high pressure hydrogen (3–5 MPa) over Co–Mo/$Al_2O_3$ catalyst [10–12]. To remove the sulfur compounds in the fuels, the HDS process is a highly efficient method. However, it is difficult to incorporate the HDS process in fuel cell applications because the fuel cell system requires an easy start-up and shut-down operation. In addition, the HDS process has the major disadvantage of requiring hydrogen addition to remove the sulfur compounds.

An adsorptive desulfurization (ADS) process can remove the sulfur compounds contained in the fuels easily. It can be operated at ordinary temperatures and frequent start-up and shut-down cycles. Activated carbon is well known as a major adsorbent for the ADS process [13–19]. Some of the activated carbon adsorbents have large pore size and high specific surface area above 1000 $m^2\ g^{-1}$ [20–22]. Zeolite is also known as a good adsorbent for the ADS process [5,23–26]. The residential fuel cell system has been already commercialized in Japan from 2009 to employ the ADS process [27]. Nevertheless, the used adsorbent needs to be replaced approximately every year due to the limit of adsorption capacity [28,29]. It is difficult to secure enough adsorption capacity until the equipment lifetime [30,31]. In Europe and North America, natural gas is transported and distributed directly by pipeline. Some kinds of sulfur compounds, *e.g.* thiols (*tert*-butanethiol, methanethiol, and the other thiols), sulfides (dimethyl sulfide, diethyl sulfide, and the other sulfides), carbonyl sulfide, and hydrogen sulfide, are contained in natural gas. In this case, it is necessary to use adsorbents corresponding to the respective sulfur compounds [32]. Hence, the adsorptive method is unsuitable for the desulfurization of the pipeline distributed natural gas. Therefore, the development of easy and efficient sulfur removal methods from the pipeline natural gas is desired instead of the HDS and ADS processes. A catalytic decomposition desulfurization (CDS) process is considered an alternative. Ziolek et al. studied the catalytic decomposition of ethanethiol, dimethyl sulfide, and thiophene over modified zeolites and reported the strength of Brønsted acidity of zeolite influences the activity and selectivity [33,34].

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* Corresponding author. Tel.: +81 422 37 3757; fax: +81 422 37 3871.
*E-mail address:* satokawa@st.seikei.ac.jp (S. Satokawa).

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Additionally, Koshelev et al. reported that γ-$Al_2O_3$ decomposes dimethyl sulfide to hydrogen sulfide at 450–500 °C [35].

In this study, we have focused on the catalytic decomposition of methanethiol which is abundantly contained in the pipeline natural gas into hydrogen sulfide and hydrocarbons ($CH_3SH \rightarrow H_2S +$ hydrocarbons). The hydrogen sulfide converted from methanethiol can be removed as a solid zinc sulfide "ZnS" to react with ZnO in the downstream of the decomposition catalyst bed. The decomposition catalyst and the desulfurization agent are supposed to be incorporated into the preheating compartment of steam reforming in the CDS process. Thereby, this process can be operated at 300–400 °C by the utilization of surplus heat from the preheating. Additionally, in the case of solid oxide fuel cell (SOFC) systems, the CDS process can be operated approximately at 500 °C to use the exhaust heat derived from SOFC because the operating temperature of cell stack is significantly high.

Recently, Huguet et al. have reported that methanethiol decomposes to hydrogen sulfide and some hydrocarbons over some hydrogen form zeolites above 500–600 °C without the hydrogen addition [36,37]. However, the decomposition reaction of methanethiol over conventional metal oxides has not been reported. Therefore, in the present study, catalytic decomposition of methanethiol into hydrogen sulfide without the hydrogen addition over various metal oxides at the moderate temperature range of 200-500 °C has been examined. In addition, the reaction scheme of methanethiol decomposition over $TiO_2$ which exhibits the high catalytic activity in the present study has been elucidated.

## 2. Experimental

### 2.1. Catalyst

Catalysts tested in this study were obtained from various suppliers. $TiO_2$ (JRC-TIO-12), $CeO_2$ (JRC-CEO-1), MgO (JRC-MGO-4), $SiO_2$ (JRC-SIO-6), and $ZrO_2$ (JRC-ZRO2) were supplied by Catalysis Society of Japan. ZnO (ActiSorb S2) was supplied by Clariant Catalysts Japan. $Al_2O_3$ was prepared by the heat-treatment at 600 °C for 2 h in air of pseudo-böehmite (Catapal B) supplied by Sasol Ltd. $La_2O_3$ and $Nb_2O_5$ were purchased from Kanto Chemical Co. Inc. CaO was obtained by the heat-treatment at 900 °C for 2 h in air of $CaCO_3$ purchased from Wako Pure Chemical Industries Ltd. All catalysts were calcined at 500 °C for 1 h prior to the catalytic activity tests and the characterization. $TiO_2$ samples having different surface areas were prepared by the heat treatment of the $TiO_2$ (JRC-TIO-12) at 500, 600, 700, and 800 °C for 2 h in air.

### 2.2. Activity test

Catalytic activity test was carried out by using a fixed-bed flow reactor under atmospheric pressure at 300 °C and 500 °C. The catalyst powders were pelletized, crushed, and sieved to 150–250 μm. The obtained pellet (500 mg) was put in the quartz reaction tube (I.D. 6 mm) and then heated at 500 °C for 1 h in nitrogen gas flow as a pretreatment. As a reaction gas mixture, 10 ppm of methanethiol ($CH_3SH$) balanced by nitrogen was continuously flowed in the reaction tube. The total gas flow rate was adjusted to 500 $cm^3\ min^{-1}$. Concentrations of sulfur compounds and hydrocarbons in the effluent gas were analyzed by a gas chromatograph (GC-8APF, Shimadzu) equipped with a flame photometric detector (FPD) and a flame ionization detector (FID), respectively. The effluent gas was analyzed every 10 min in order to evaluate the reaction behavior for an initial 240 min.

Effect of the reaction temperature on methanethiol decomposition over $TiO_2$ was studied at the temperature range of 200–500 °C. Prior to the activity test, 10 ppm of methanethiol balanced by nitrogen gas was continuously flowed in the reaction tube at 500 °C for 18 h as the pretreatment in order to evaluate the catalytic performance under stable conditions, and the total gas flow rate of reaction gas was adjusted to 500 $cm^3\ min^{-1}$. The reaction temperature was decreased from 500 °C to 200 °C at a cooling rate of 1 °C $min^{-1}$ and the effluent gas was analyzed every 25 °C.

Effect of the specific surface area of $TiO_2$ on methanethiol decomposition was investigated by using various $TiO_2$ catalysts calcined in air at 500–800 °C. Activity test was carried out under the above mentioned condition at 300 °C without any pretreatment.

The stability tests of methanethiol decomposition over $TiO_2$ at 300 °C and 500 °C for 100 h were conducted. Two hundred milligrams of $TiO_2$ was put in the quartz reaction tube and 100 ppm of methanethiol balanced by nitrogen gas was flowed in the reaction tube. The total gas flow rate was adjusted to 200 $cm^3\ min^{-1}$.

### 2.3. Catalyst characterization

The specific surface areas of catalysts were determined by the conventional BET method by using a nitrogen adsorption apparatus (BELSORP-mini, BEL Japan). Catalysts were heated at 150 °C for 2 h in helium as a pretreatment. The crystalline phases of catalysts were measured by using an X-ray diffraction (XRD, Ultima-IV, Rigaku) equipped with Cu Kα radiation operated at 40 kV and 40 mA and with a scanning speed of 2°$min^{-1}$. The thermogravimetry (TG) and differential thermal analyses (DTA) of the spent catalysts were carried out by using a TG-DTA apparatus (Thermo plus EVO II, Rigaku). Catalysts (15 mg) were put in a platinum cell and were heated from room temperature to 500 °C in atmospheric condition. The temperature programmed oxidation (TPO) analysis of the spent catalysts was conducted using a catalyst analyzer (BELCAT, Bell Japan) with a mass spectrometer (OmniStar, Pfeiffer). Catalysts (50 mg) were put in the quartz tube and then heated to 500 °C at a heating rate of 10 °C $min^{-1}$ in 20% oxygen balanced by argon gas. The amounts of sulfur and carbon species contained in the spent catalysts were measured by using an elemental analysis apparatus (vario MICRO cube, Elementar Analysensysteme GmbH). Small amounts of the spent catalysts (2 mg) were put in a small tin cell and then heated to 1400 °C in 20% oxygen balanced by helium gas. Sulfanilic acid (Merck KGaA) was used as a standard substance of sulfur and carbon components.

Analysis of adsorbed species on the catalyst surface under the reaction condition was carried out by *in-situ* Fourier transform infrared spectroscopy (FTIR) with a transmission method by using an infrared spectroscopy (FT/IR-4100, JASCO) equipped with a glass reaction cell (Makuhari Rikagaku Garasu Inc.). The measurement range of IR spectra was 1100–4000 $cm^{-1}$, and the $CaF_2$ crystal was used as a window material of the glass reaction cell. A thin disk of $TiO_2$ catalyst having *ca.* 0.2 mm thickness was molded and was set in the glass reaction cell. After that, it was heated at 500 °C for 1 h in nitrogen gas flow. After cooling, the background spectrum was recorded at 50 °C in nitrogen atmosphere. Thereafter, 100 ppm of methanethiol balanced by nitrogen was continuously flowed in the reaction cell at 50 °C for 30 min, and subsequently it was replaced to nitrogen gas. After the adsorption stage, the catalyst disk was heated at 50 °C, 300 °C, and 500 °C for 30 min, and then cooled down to 50 °C in nitrogen atmosphere. After the adsorption and reaction treatments, IR spectra were recorded at 50 °C in nitrogen atmosphere.

## 3. Results

### 3.1. Catalyst characterization

The specific surface areas of catalysts tested in the present study are summarized in Table 1. Specific surface areas of $Al_2O_3$, $CeO_2$, $SiO_2$, $TiO_2$, and $ZrO_2$ were more than 100 $m^2\ g^{-1}$ and those of $Nb_2O_5$ and CaO was less than 10 $m^2\ g^{-1}$. The crystalline phase of $TiO_2$ was assigned to anatase.