



# Methanol oxidative decomposition over zirconia supported silver catalyst and its reaction mechanism



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## ABSTRACT

To develop a new catalyst for catalytic decomposition of volatile organic compounds (VOCs), the activity of various oxide supported silver (Ag) based catalysts for methanol (MeOH) oxidation reaction have been evaluated. Based on the activity evaluation, zirconia (ZrO<sub>2</sub>) is considered to be a substitute to ceria (CeO<sub>2</sub>) as a support material. The ZrO<sub>2</sub> supported catalyst loading Ag component can oxidize MeOH to CO<sub>2</sub> completely, while the main product is CO for MeOH oxidation over pure ZrO<sub>2</sub>. In the present work, 2.0 wt.% Ag/ZrO<sub>2</sub> exhibits excellent activity comparable to Ag/CeO<sub>2</sub>. Furthermore, according to *in situ* FT-IR analysis over Ag/ZrO<sub>2</sub> and pure ZrO<sub>2</sub>, it is considered that the methoxy, formate, and bicarbonate species adsorbed on the ZrO<sub>2</sub> surface are intermediate species. We thus deduce that Ag component significantly enhances the oxidation step of methoxy species to CO<sub>2</sub> via formate species, leading to the complete oxidation of MeOH to CO<sub>2</sub> over Ag/ZrO<sub>2</sub> catalyst.

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## 1. Introduction

Volatile organic compounds (VOCs) are recognized as air pollutants that cause photochemical smog, ground-level ozone, sick house syndrome, and chemical sensitivity [1–4]. Thus, detoxification treatment of VOCs is required and the emission regulation of VOCs is established by Air Pollution Control Act in any countries. Among VOCs, formaldehyde is produced by partial oxidation of methanol (MeOH) and used as organic solvents, coating materials, and resinous raw materials [5]. Various methods: flame combustion, catalytic decomposition using plasma, photocatalytic decomposition, adsorbent-based methods, have been intensively investigated for the effective abatement of VOCs. The catalytic combustion process has advantageous features for VOCs removal as compared with other methods [6]. In the catalytic combustion process, the selection of active metal materials is an important factor for the development of catalysts. Transition metal catalysts are

more efficient on a cost basis as compared with precious metal ones; however, the former exhibits lower activity for VOCs combustion [7–9]. On the other hand, precious metal catalysts can achieve the complete oxidation at low temperature due to their high activity [10–13]. For the MeOH oxidative decomposition process, Pt [14], Ru [15,16], Au [17–19], and Ag [20–25] metals have been well researched as active metals. In addition, transition metal based catalysts using the Cu [26–29], Mo [30], Ni [31,32], and V [33–36] metals have been also reported. Cerium oxide (ceria, CeO<sub>2</sub>) is considered an attractive support due to its high oxygen storage capacity (OSC) [37,38]. Actually, many researchers reported that ceria supported precious metal catalysts exhibit high activity for formaldehyde, MeOH, and other VOCs oxidation reactions [7,8,13,17,19,24,37,39]. However, the cost of precious metal catalysts and their catalytic degradation will become serious problems for the practical application. Additionally, the supply risk of precious metals and rare-earth metals including cerium is a serious international problem. Thus, several oxides such as TiO<sub>2</sub> [18,40], SiO<sub>2</sub> [26], Al<sub>2</sub>O<sub>3</sub> [23,41], ZnO [18,28], FeOx [42], ZrO<sub>2</sub> [15,16,26,29,30], CeO<sub>2</sub>-ZrO<sub>2</sub> [14,24], and mesoporous SiO<sub>2</sub> [19,27] have been investigated as support materials and a novel catalyst

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for the oxidation process of MeOH as well as other VOCs have been studied [43].

Based on this background, in the present study, we have focused on a supported silver (Ag) catalyst for the oxidation of MeOH which convert to formaldehyde easily. In particular, we have studied zirconium oxide (zirconia,  $ZrO_2$ ) supported Ag ( $Ag/ZrO_2$ ) catalysts, because the  $ZrO_2$  support is considered to be a suitable alternative candidate to  $CeO_2$  and also there is no report of the MeOH oxidative decomposition over  $Ag/ZrO_2$  catalyst. Specifically, the comparative study of the catalytic activity of  $Ag/ZrO_2$  with other several oxide supported metal catalysts for MeOH oxidation has been conducted. Furthermore, *in-situ* Fourier transform infrared spectroscopy (FT-IR) analysis of the catalyst have been undertaken to obtain the insight on the reaction mechanism for MeOH oxidation over  $Ag/ZrO_2$  catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

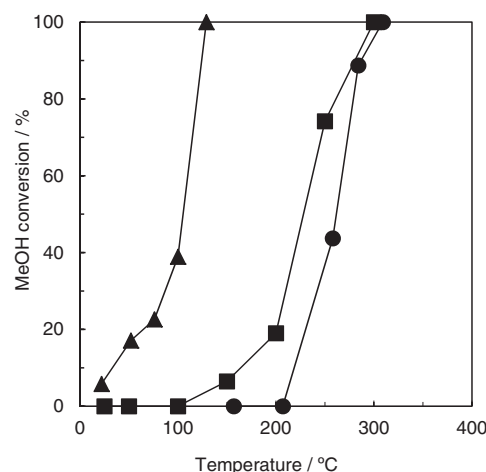
The various metal oxide supported metal catalysts were prepared by the impregnation method [44]. The following metal oxides were used as support materials:  $ZrO_2$  (JRC-ZRO-3 and JRC-ZRO-2),  $CeO_2$  (JRC-CEO-3), MgO (JRC-MGO-4 500A) provided by the Catalysis Society of Japan;  $MnO_2$  (MN-280) provided by Clariant Catalysts (Japan) K.K.;  $Al_2O_3$  prepared from aluminum hydroxides (Catapal B) provided by Sasol Ltd. by the heat treatment in air at 600 °C for 2 h. An aqueous solution of  $AgNO_3$  provided by Wako Pure Chemical Industries, Ltd. was used as the Ag source. In addition,  $Pt(NH_3)_2(NO_2)_2$  nitric acid solution provided by Kojima Chemical Co., Ltd. and  $Co(NO_3)_2$  hexahydrate,  $Cu(CH_3COO)_2$  monohydrate, and  $SnCl_2$  dihydrate provided by Wako Pure Chemical Industries, Ltd., were used as each metal source. The loading of Ag metal was adjusted to 0.5–5.0 wt.% in the metallic form. Each metal oxide powder was impregnated with an aqueous solution of the metal component of interest. The mixture was stirred at room temperature under 13 kPa for 2 h and then the solution was evaporated sufficiently on a water bath at 80 °C under 40 kPa. The obtained samples were dried in air at 110 °C and then calcined in air at 500 °C for 2 h. Subsequently, the obtained powders were pressed, crushed, and sieved to particle size of 150–250  $\mu m$  for the catalytic activity tests of MeOH oxidation.

### 2.2. Catalytic activity test

The evaluation of catalytic performance for MeOH oxidation was conducted using a fixed-bed flow reactor. The prepared catalyst (0.2 g) was housed in the quartz tube reactor with a diameter of 6 mm and a reaction gas mixture (700 ppm MeOH/20%  $O_2$ /He balance) was fed to the catalyst bed at a total flow rate of 300 mL/min (gas hourly space velocity: 100,000  $L kg^{-1} h^{-1}$ ). The compositions of the inlet and outlet gases were analyzed using a gas chromatograph equipped with a flame ionization detector (Shimadzu, GC-8A). A SHINCARBON ST 50–80 column (Shinwa Chem. Ind.) and a methanizer accessory were used to determine the amount of MeOH, CO, and  $CO_2$ .

### 2.3. Catalyst characterization

The specific surface area of each support oxide without and with the heat treatments and each prepared catalyst was determined by  $N_2$  adsorption measurement at 77 K by the conventional BET method using a Microtrac BEL BELSORP-mini II instrument. Prior to  $N_2$  adsorption, the sample was degassed at 200 °C for 2 h in order to remove the moisture adsorbed on the surface and inside the porous network.



**Fig. 1.** Catalytic activity of various oxides for MeOH oxidation: (●)  $ZrO_2$  (JRC-ZRO-3), (■)  $CeO_2$  (JRC-CEO-3), (▲)  $MnO_2$  (MN-280); reaction conditions: 700 ppm MeOH/20%  $O_2$ /He balance; W/F: 0.04  $g h cm^{-3}$ .

To identify the crystalline structure of each support oxide and each prepared catalyst, the powder X-ray diffraction (XRD) pattern was measured using a Rigaku Ultima IV instrument equipped with a  $Cu K\alpha$  radiation source ( $\lambda = 0.154 nm$ ). The typical working conditions such as an acceleration voltage and current were 40 kV and 20 mA with a scanning speed of 1°  $min^{-1}$ .

Transmission electron microscopy (TEM) of 2.0 wt.%  $Ag/ZrO_2$  and 2.0 wt.%  $Ag/CeO_2$  was performed using a JEOL JEM-2100F operated at 200 kV. The samples were dispersed by ultrasonic in ethanol followed by deposition of the resultant suspension onto a standard Cu grid covered with a holey carbon film.

To elucidate the adsorbed species and intermediates during MeOH oxidation over pure  $ZrO_2$  and  $Ag/ZrO_2$ , *in-situ* Fourier transform infrared spectroscopy (FT-IR) analysis was conducted using a SHIMADZU FTIR-8300 equipped with a glass reaction cell (Makuhari Rikagaku Garasu Inc.). Thin disks of each sample were made and placed in the FT-IR cell. For the measurement of  $Ag/ZrO_2$ , the spectrum was recorded under 20%  $O_2$ /He at the temperature range of room temperature to 125 °C after the pre-treatments as follows: heat-treatment in 20%  $O_2$ /He at 200 °C for 2 h, and then cooling to room temperature. Subsequently, a gaseous mixture of 1% MeOH/20%  $O_2$ /He balance was fed the samples to adsorb the MeOH-derived species on the sample surface. The interior of reaction cell was then purged with 20%  $O_2$ /He for 15 min. For the measurement of pure  $ZrO_2$ , the adsorption step of MeOH was carried out at 200 °C and the spectrum was recorded under 20%  $O_2$ /He gaseous condition at the temperature range of 200–300 °C after the pretreatment as mentioned above. For the both measurements, prior to the MeOH adsorption step, back ground spectrum was recorded in 20%  $O_2$ /He at room temperature or 200 °C, respectively. The IR measurement was operated at a resolution of 4  $cm^{-1}$ , and 45 scans were collected for each spectrum.

## 3. Results and discussion

### 3.1. Catalytic activity for MeOH oxidation

#### 3.1.1. Activity of various oxides

Firstly, the catalytic activity of the representative pure oxides for MeOH oxidative decomposition has been evaluated. Fig. 1 shows the temperature dependence of MeOH conversion for MeOH oxidation over  $ZrO_2$  (JRC-ZRO-3),  $CeO_2$  (JRC-CEO-3), and  $MnO_2$  (MN-280) oxides as-obtained. Among them, pure  $MnO_2$  exhibited much higher activity than  $ZrO_2$  and  $CeO_2$ . As shown in Table 1,

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