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Formaldehyde production via partial oxidation of methanol over oxides of Cr, Mo and W supported on ceria-zirconia

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Abstract: Oxides of chromium (Cr), molybdenum (Mo), or tungsten (W) were supported on mixed oxides of cerium and zirconium (CeO₂-ZrO₂) by an incipient wetness impregnation process, and used to investigate their activities for partial oxidation of methanol. High Resolution Transmission Electron Microscope (HR-TEM) revealed that nanoparticles of Cr₂O₃, MoO₃ and WO₃ were formed on the CeO₂-ZrO₂ support. The particle sizes of Cr₂O₃, MoO₃ and WO₃ were 2-4, 3-6 and 4-5 nm, respectively. As a result of partial oxidation of methanol at 275 – 450 ℃, formaldehyde (CH₂O) was obtained as the major product over all these catalysts. Cr₂O₃ supported on CeO₂-ZrO₂ produced both CO and CO₂ along with H₂ production, while MoO₃ and WO₃ on CeO₂-ZrO₂ support generated only CO as a by-product. It was found that MoO₃ supported on CeO₂-ZrO₂ showed the highest methanol conversion and CH₂O yield among these three catalysts.

1. Introduction
Partial oxidation of methanol (POM) has been investigated in view of hydrogen production [1-3] and formation of formaldehyde (CH₂O) via oxidative dehydrogenation (ODH) [4-6]. Transition metal elements in the 6B group, chromium (Cr), molybdenum (Mo) and tungsten (W), are highly related with these kinds of reactions involving methanol in the literature. For example, Cr₂O₃ supported on zinc oxide was used for methanol synthesis from CO and H₂ at high pressure [7, 8]. Because catalysts have possibility to be effective for the reverse reaction, it can be assumed that Cr₂O₃ based catalysts can also be used for H₂ production from methanol, which is a reverse reaction of the methanol synthesis. Similarly, Mo based catalysts, which are MoO₃ and Fe₂(MoO₄)₃, have been investigated for formaldehyde production via ODH of methanol [9, 10], and tungsten oxide (WO₆) supported on TiO₂ was used for dehydration of methanol to produce dimethyl ether [11].

Recently, mixed oxides of CeO₂-ZrO₂ (CZ) have attracted attention due to their high oxygen mobility property [12]. Bake et al. compared the activity of gold (Au) catalysts supported on ZrO₂, CeO₂-ZrO₂, or CeO₂-ZrO₂-TiO₂, and found that Au supported on CeO₂-ZrO₂ exhibited the highest activity toward hydrogen generation via POM [1]. They suggested that the contribution of oxidized..
gold particles and redox property of CeO\textsubscript{2}-ZrO\textsubscript{2} brought about the high conversion of methanol and the high selectivity of H\textsubscript{2} production. In this study, oxides of Cr, Mo and W were synthesized on a CeO\textsubscript{2}-ZrO\textsubscript{2} (CZ) mixed support and their catalytic performance for methanol partial oxidation have been investigated in order to clarify the activities of 6B group elements supported on CeO\textsubscript{2}-ZrO\textsubscript{2} (CZ) toward POM and ODH reaction.

\begin{align}
\text{POM reaction:} & \quad \text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2 \quad (1) \\
\text{ODH reaction:} & \quad \text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \quad (2)
\end{align}

2. Experimental

2.1. Catalyst Preparation

CeO\textsubscript{2}-ZrO\textsubscript{2} mixed support was prepared by a simple mechanical mixing of powders of CeO\textsubscript{2} and ZrO\textsubscript{2} [1]. Powders of CeO\textsubscript{2} (Acros) and ZrO\textsubscript{2} (Aldrich) with a weight ratio of 3:1 were ultrasonically homogenized in water, and then dried at 120 °C in an oven overnight. Cr, Mo or W (1 mass% of each transition metal) was supported on CeO\textsubscript{2}-ZrO\textsubscript{2} by an incipient wetness impregnation process using aqueous solution of Cr(NO\textsubscript{3})\textsubscript{2}·9H\textsubscript{2}O (Aldrich), (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}·4H\textsubscript{2}O (Aldrich) or (NH\textsubscript{4})\textsubscript{6}H\textsubscript{2}W\textsubscript{12}O\textsubscript{40}·xH\textsubscript{2}O (Aldrich). CeO\textsubscript{2}-ZrO\textsubscript{2} support was added into the aqueous solutions of individual salts, and water was removed by rotary evaporator at 40 °C and around 50 mbar. After further drying at 110 °C for 2 h in an oven, the powders were calcined in the air at 500 °C for 5 h at a ramping rate of 5 °C min\textsuperscript{-1}. CeO\textsubscript{2}-ZrO\textsubscript{2} supporting oxides of Cr, Mo and W are named CrO\textsubscript{x}/CZ, MoO\textsubscript{x}/CZ and WO\textsubscript{x}/CZ, respectively, throughout this manuscript.

2.1.1. Characterization. Crystal structures of the samples were characterized by X-ray diffraction (XRD) and High Resolution Transmission Electron Microscope (HR-TEM). TEM was also used to characterize size and shape of particles. Content of Cr, Mo or W was analyzed by X-ray Fluorescence (XRF). Oxidation states of Cr, Mo or W were analyzed by X-ray Photoelectron Spectroscopy (XPS). Adsorption and desorption isotherm of N\textsubscript{2} was analyzed at 77 K after degassing at 200 °C for 2 h under vacuum, and analyzed by Brunauer Emmette Teller (BET) method in order to evaluate specific surface area.

2.1.2. Catalyst activity measurement setup. Partial oxidation of methanol was carried out in a system (PID Eng & Tech, Spain) with a heat box and a continuous fixed bed reactor of quartz (o.d. = 6 mm), as shown in Figure 1. The catalytic reactions were examined at atmospheric pressure in a temperature interval between 275 and 450 °C according to conditions of previous experiments done by Bake et al [1]. The reactor was charged with 100 mg of catalyst. The heat box was kept at 150 °C to avoid inline condensation. Methanol and oxygen were fed to the reactor while being diluted with helium. O\textsubscript{2}/Methanol molar ratio and gas hourly space velocity (GHSV) were 0.5 and 30,000 ml g\textsuperscript{-1} h\textsuperscript{-1}, respectively, for all reactions. Residuals of methanol (CH\textsubscript{3}OH) and oxygen (O\textsubscript{2}) and products, which were formaldehyde (CH\textsubscript{2}O), carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}) and hydrogen (H\textsubscript{2}) were quantitatively analyzed by a gas chromatograph (GC, Hewlett Packard HP6890) with separation columns of Molecular sieve 5A and Porapak QS.
Figure 1. Schematic image of partial oxidation of methanol (POM) reaction system.

Conversion of reactant and selectivity of products were calculated as follows.

\[
CH_3OH \text{ conversion (\%)} = \left( \frac{\text{mol. flow of CH}_3\text{OH in} - \text{mol. flow of CH}_3\text{OH out}}{\text{mol. flow of CH}_3\text{OH in}} \right) \times 100
\]

\[
O_2 \text{ conversion (\%)} = \left( \frac{\text{mol. flow of } O_2 \text{ in} - \text{mol. flow of } O_2 \text{ out}}{\text{mol. flow of } O_2 \text{ in}} \right) \times 100
\]

\[
CH_2O \text{ selectivity (\%)} = \left( \frac{\text{mol. flow of CH}_2O}{\text{mol. flow of CH}_3\text{OH consumed}} \right) \times 100
\]

\[
CO \text{ selectivity (\%)} = \left( \frac{\text{mol. flow of CO}}{\text{mol. flow of CH}_3\text{OH consumed}} \right) \times 100
\]

\[
CO_2 \text{ selectivity (\%)} = \left( \frac{\text{mol. flow of CO}_2}{\text{mol. flow of CO}} \right) \times 100
\]

\[
H_2 \text{ selectivity (\%)} = \left( \frac{2 \times \text{mol. flow of } H_2}{\text{mol. flow of CH}_3\text{OH consumed}} \right) \times 100
\]

3. Results and Discussion

3.1. Characterization

XRD patterns of CeO$_2$-ZrO$_2$ (CZ) support, CrO$_x$/CZ, MoO$_x$/CZ and WO$_x$/CZ are shown in Figure 2. XRD patterns of the catalysts do not show any characteristic peaks assigned to the oxides of Cr, Mo or W, which were impregnated on the support. This may arise from the fact that the mass% of each transition metal is 1%, very low concentration which may cause formation of very small crystallites, and that may be under the detection limit of the XRD equipment. And/or the peaks are so small that it is shaded under the ceria and zirconia peaks. Later on HR-TEM images confirmed the formation of small nano particles (< 5 nm) of transition metals over CZ support.

In order to identify crystal structures of CrO$_x$, MoO$_x$ and WO$_x$ on the support, their particles were observed by HR-TEM as shown in Figure 3. HR-TEM of CrO$_x$/CZ, as shown in Figure 3(a), revealed that CrO$_x$ has d space of 3.64 Å corresponding to (0 1 2) plane of Cr$_2$O$_3$. HR-TEM also showed that the particle size of Cr$_2$O$_3$ was smaller than 5 nm. HR-TEM of MoO$_x$/CZ showed that MoO$_3$ was formed on the support because d space of the MoO$_3$ was 6.9 Å corresponding to MoO$_3$ (0 0 1). The particle size of MoO$_3$ was around 5 nm. HR-TEM and Fast Fourier Transform (FFT) image of WO$_x$/CZ also revealed that WO$_3$ was formed as shown in Figure 3(c). The particle size of WO$_3$ was 4 - 5 nm.

XPS profiles shown in Figure 4 are consistent with the identification by HR-TEM, which shows the formation of Cr$_2$O$_3$, MoO$_3$ and WO$_3$ over CrO$_x$/CZ, MoO$_x$/CZ and WO$_x$/CZ, respectively. From above results, it is clarified that fine and well dispersed nano particles of Cr$_2$O$_3$, MoO$_3$ and WO$_3$ were
formed on CrO\textsubscript{x}/CZ, MoO\textsubscript{x}/CZ and WO\textsubscript{x}/CZ catalysts, respectively, via the catalyst preparation process.

Figure 2. XRD patterns of (a) CeO\textsubscript{2}-ZrO\textsubscript{2} support, (b) CrO\textsubscript{x}/CZ, (c) MoO\textsubscript{x}/CZ and (d) WO\textsubscript{x}/CZ.

Figure 3. HR-TEM images of (a) CrO\textsubscript{x}/CZ, (b) MoO\textsubscript{x}/CZ and (c) WO\textsubscript{x}/CZ with Fast Fourier Transform (FFT) image.

Figure 4. XPS profiles of (a)CrO\textsubscript{x}/CZ, (b)MoO\textsubscript{x}/CZ and (d)WO\textsubscript{x}/CZ with peak separation analysis.

From the results of XRF, the contents of Cr, Mo and W in each sample were estimated as shown in Table 1. The content of the active material, which was Cr, Mo or W, in the catalysts was
approximately 1 mass%, which means the catalysts were prepared successfully according to the desired mass% of the active metal on the support. Specific Surface Area (SSA) of the samples are also shown in Table 1, where all the catalysts have similar values, which are close to the support CeO$_2$-ZrO$_2$ SSA value.

| Sample (M) | CrO$_x$/CZ (Cr) | MoO$_x$/CZ (Mo) | WO$_x$/CZ (W) | CeO$_2$-ZrO$_2$ support |
|-----------|-----------------|-----------------|---------------|-------------------------|
| M content (mass%) | 0.95           | 1.08           | 1.09          | 0                       |
| Surface area (m$^2$/g) | 6.3             | 4.3            | 5.5           | 7.4                     |

**3.2. Partial Oxidation of Methanol (POM)**

Temperature dependency of CH$_3$OH and O$_2$ conversion and selectivity of formaldehyde (CH$_2$O), CO$_2$, CO and H$_2$ over three catalysts are shown in Figure 5. Over all catalysts, formaldehyde (CH$_2$O) was obtained as the major product, suggesting that oxidative dehydrogenation of methanol (reaction 2) is mainly catalyzed over these oxides of 6B group elements supported on CeO$_2$ and ZrO$_2$.

CO was also generated as a by-product over these catalysts with the increase of reaction temperature. CO might be generated by thermal decomposition of CH$_3$OH to CO and H$_2$ (reaction 9) or oxidation of CH$_2$O to CO and H$_2$O (reaction 10). If thermal decomposition of CH$_3$OH (reaction 9) took place, H$_2$ selectivity must have same value of CO selectivity. The observed H$_2$ selectivity is, however, lower than CO selectivity, suggesting that H$_2$ was generated by other reactions. So it can be considered that CO was generated by oxidation of CH$_2$O (reaction 10). In particular, behaviors of CH$_2$O selectivity (decreasing) and CO selectivity (increasing) are showing opposite trends on CrO$_x$/CZ with the increase of temperature, as shown in Figure 5(a), which suggests that the oxidation decomposition of the CH$_2$O is happening over the surface to produce CO according to (reaction 10).

On both MoO$_x$/CZ and WO$_x$/CZ, CO selectivity increased with temperature, while very little H$_2$ and CO$_2$ was generated. The behavior of CO and H$_2$ generation on MoO$_x$/CZ and WO$_x$/CZ is consistent with oxidation of CH$_2$O (reaction 10). Only CrO$_x$/CZ produced considerable amount of both CO$_2$ and H$_2$ as by-products, indicating that partial oxidation of methanol (reaction 1) or water gas shift reaction (reaction 11) took place over CrO$_x$/CZ.

Mole of generated H$_2$, CO and CO$_2$ were almost same among them on the CrO$_x$/CZ. Because the amount of H$_2$ generated via the partial oxidation of methanol (reaction 1) is theoretically double of the amount of CO$_2$, the partial oxidation reaction can be assumed not to have taken place on CrO$_x$/CZ. Therefore, it can be considered that water gas shift reaction (reaction 11) took place from CO and H$_2$O generated by oxidation of CH$_2$O. When about a half of the generated CO reacts with H$_2$O, the final product have same amount of CO, CO$_2$ and H$_2$, and the selectivity of CO, CO$_2$ and H$_2$ on CrO$_x$/CZ can be explained over this catalyst.

In regard to formaldehyde production, CH$_3$OH conversions and CH$_2$O yields of the three catalysts were compared as shown in Figure 6. Among the three catalysts, MoO$_x$/CZ showed the highest methanol conversion and CH$_2$O yield at all the investigated temperature range. The maximum yield of formaldehyde was observed at 375 °C for MoO$_x$/CZ.

The catalysis of Cr$_2$O$_3$ on CeO$_2$-ZrO$_2$ is similar to that of CrO$_3$ supported on SiO$_2$, which obtained formaldehyde as the main product and acetic acid, CO and CO$_2$ as by-products [13]. The activity toward ODH reaction might be due to the nature of chromium oxides.

We have observed that MoO$_x$/CZ showed the highest activity toward ODH of CH$_3$OH to produce CH$_2$O (reaction 2) among these three catalysts under investigation as well as reported Mo based catalysts with high activities for formaldehyde production in literature [9, 10, 14-17].

Although tungsten oxide (WO$_3$) has been reported as a catalyst for dehydration of CH$_3$OH (feed pure CH$_3$OH) to obtain dimethyl ether [11], in this study CH$_2$O was obtained as a main product via
ODH of CH$_3$OH over WO$_x$/CZ. The difference of the activity and selectivity of WO$_x$/CZ catalyst might be caused by the use of CZ support and the presence of oxygen to perform partial oxidation.

\[
\text{Methanol thermal decomposition: } \text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 \quad (9) \\
\text{Oxidation of formaldehyde: } 2\text{CH}_2\text{O} + \text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2\text{O} \quad (10) \\
\text{Water gas shift: } \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (11)
\]

**Figure 5.** Conversion and selectivity of partial oxidation of methanol over (a) Cr$_x$/CZ, (b) Mo$_x$/CZ and (c) WO$_x$/CZ.

**Figure 6.** Temperature dependency of (a) methanol conversion and (b) formaldehyde selectivity over catalysts.

**4. Conclusions**

Oxides of 6B group elements, Cr, Mo or W, were supported on mixed oxides of Ce and Zr in order to investigate their catalytic activity toward partial oxidation of methanol. Nanoparticles of Cr$_2$O$_3$, MoO$_3$ or WO$_3$ were successfully synthesized on the support and all these catalysts resulted in the selective formation of formaldehyde (CH$_2$O). The MoO$_3$ supported on CeO$_2$-ZrO$_2$ showed the highest methanol conversion and CH$_2$O yield among these three catalysts.
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