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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 or 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 °C, 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.

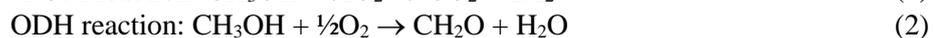
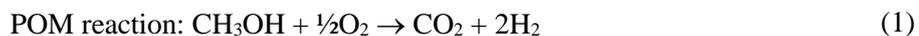
1. Introduction

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 be also 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 (WO_x) 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 CeO₂-ZrO₂ brought about the high conversion of methanol and the high selectivity of H₂ production. In this study, oxides of Cr, Mo and W were synthesized on a CeO₂-ZrO₂ (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 CeO₂-ZrO₂ (CZ) toward POM and ODH reaction.



2. Experimental

2.1. Catalyst Preparation

CeO₂-ZrO₂ mixed support was prepared by a simple mechanical mixing of powders of CeO₂ and ZrO₂ [1]. Powders of CeO₂ (Acros) and ZrO₂ (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 CeO₂-ZrO₂ by an incipient wetness impregnation process using aqueous solution of Cr(NO₃)₂·9H₂O (Aldrich), (NH₄)₆Mo₇O₂₄·4H₂O (Aldrich) or (NH₄)₆H₂W₁₂O₄₀·xH₂O (Aldrich). CeO₂-ZrO₂ 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⁻¹. CeO₂-ZrO₂ supporting oxides of Cr, Mo and W are named CrO_x/CZ, MoO_x/CZ and WO_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 N₂ 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. O₂/Methanol molar ratio and gas hourly space velocity (GHSV) were 0.5 and 30,000 ml g⁻¹ h⁻¹, respectively, for all reactions. Residuals of methanol (CH₃OH) and oxygen (O₂) and products, which were formaldehyde (CH₂O), carbon monoxide (CO), carbon dioxide (CO₂) and hydrogen (H₂) were quantitatively analyzed by a gas chromatograph (GC, Hewlett Packard HP6890) with separation columns of Molecular sieve 5A and Porapak QS.

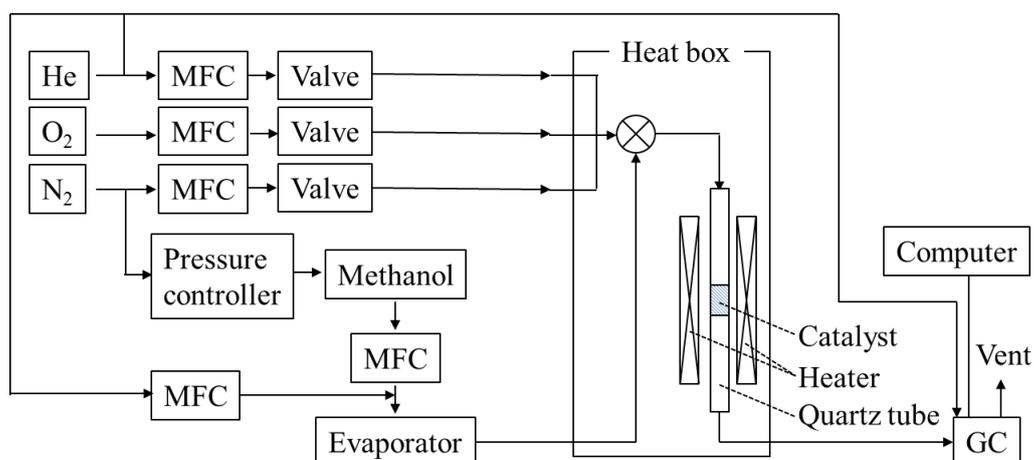


Figure 1. Schematic image of partial oxidation of methanol (POM) reaction system.

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

$$CH_3OH \text{ conversion (\%)} = \frac{\text{mol. flow of } CH_3OH_{in} - \text{mol. flow of } CH_3OH_{out}}{\text{mol. flow of } CH_3OH_{in}} \times 100 \quad (3)$$

$$O_2 \text{ conversion (\%)} = \frac{\text{mol. flow of } O_{2in} - \text{mol. flow of } O_{2out}}{\text{mol. flow of } O_{2in}} \times 100 \quad (4)$$

$$CH_2O \text{ selectivity (\%)} = \frac{\text{mol. flow of } CH_2O}{\text{mol. of } CH_3OH_{consumed}} \times 100 \quad (5)$$

$$CO \text{ selectivity (\%)} = \frac{\text{mol. flow of } CO}{\text{mol. of } CH_3OH_{consumed}} \times 100 \quad (6)$$

$$CO_2 \text{ selectivity (\%)} = \frac{\text{mol. flow of } CO_2}{\text{mol. of } CH_3OH_{consumed}} \times 100 \quad (7)$$

$$H_2 \text{ selectivity (\%)} = \frac{\text{mol. flow of } H_2}{2 \times \text{mol. of } CH_3OH_{consumed}} \times 100 \quad (8)$$

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_2O_3 . HR-TEM also showed that the particle size of Cr_2O_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_x 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_2O_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_2O_3 , MoO_3 and WO_3 were

formed on CrO_x/CZ , MoO_x/CZ and WO_x/CZ catalysts, respectively, via the catalyst preparation process.

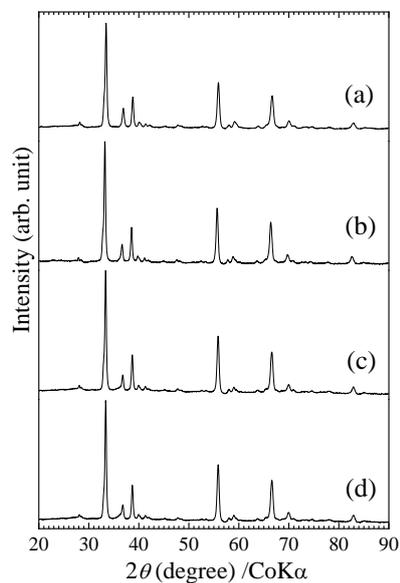


Figure 2. XRD patterns of (a) $\text{CeO}_2\text{-ZrO}_2$ support, (b) CrO_x/CZ , (c) MoO_x/CZ and (d) WO_x/CZ .

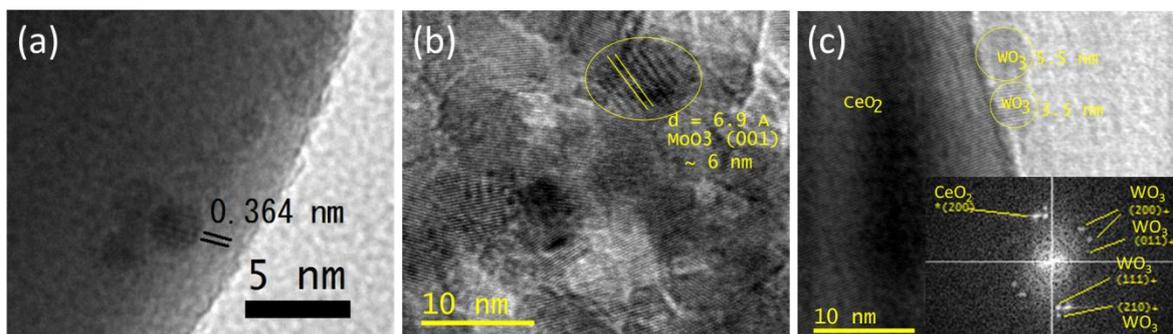


Figure 3. HR-TEM images of (a) CrO_x/CZ , (b) MoO_x/CZ and (c) WO_x/CZ with Fast Fourier Transform (FFT) image.

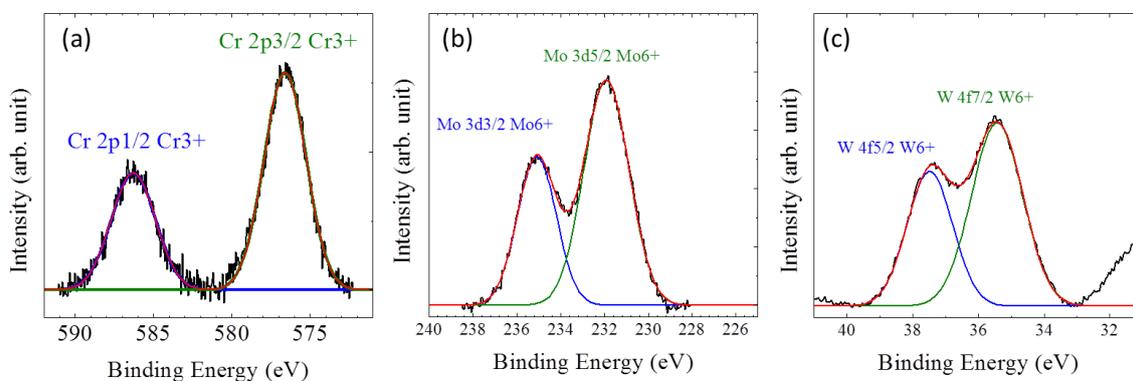


Figure 4. XPS profiles of (a) CrO_x/CZ , (b) MoO_x/CZ and (d) WO_x/CZ with peak separation analysis.

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 CeO₂-ZrO₂ SSA value.

Table 1. Content of M (M = Cr, Mo or W) and specific surface area (SSA) of catalysts.

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 CH₃OH and O₂ conversion and selectivity of formaldehyde (CH₂O), CO₂, CO and H₂ over three catalysts are shown in Figure 5. Over all catalysts, formaldehyde (CH₂O) 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 CeO₂ and ZrO₂.

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 CH₃OH to CO and H₂ (reaction 9) or oxidation of CH₂O to CO and H₂O (reaction 10). If thermal decomposition of CH₃OH (reaction 9) took place, H₂ selectivity must have same value of CO selectivity. The observed H₂ selectivity is, however, lower than CO selectivity, suggesting that H₂ was generated by other reactions. So it can be considered that CO was generated by oxidation of CH₂O (reaction 10). In particular, behaviors of CH₂O 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 CH₂O 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 H₂ and CO₂ was generated. The behavior of CO and H₂ generation on MoO_x/CZ and WO_x/CZ is consistent with oxidation of CH₂O (reaction 10). Only CrO_x/CZ produced considerable amount of both CO₂ and H₂ 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 H₂, CO and CO₂ were almost same among them on the CrO_x/CZ. Because the amount of H₂ generated via the partial oxidation of methanol (reaction 1) is theoretically double of the amount of CO₂, 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 H₂O generated by oxidation of CH₂O. When about a half of the generated CO reacts with H₂O, the final product have same amount of CO, CO₂ and H₂, and the selectivity of CO, CO₂ and H₂ on CrO_x/CZ can be explained over this catalyst.

In regard to formaldehyde production, CH₃OH conversions and CH₂O 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 CH₂O yield at all the investigated temperature range. The maximum yield of formaldehyde was observed at 375 °C for MoO_x/CZ.

The catalysis of Cr₂O₃ on CeO₂-ZrO₂ is similar to that of CrO₃ supported on SiO₂, which obtained formaldehyde as the main product and acetic acid, CO and CO₂ 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 CH₃OH to produce CH₂O (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_x) has been reported as a catalyst for dehydration of CH₃OH (feed pure CH₃OH) to obtain dimethyl ether [11], in this study CH₂O was obtained as a main product via

ODH of CH_3OH 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.

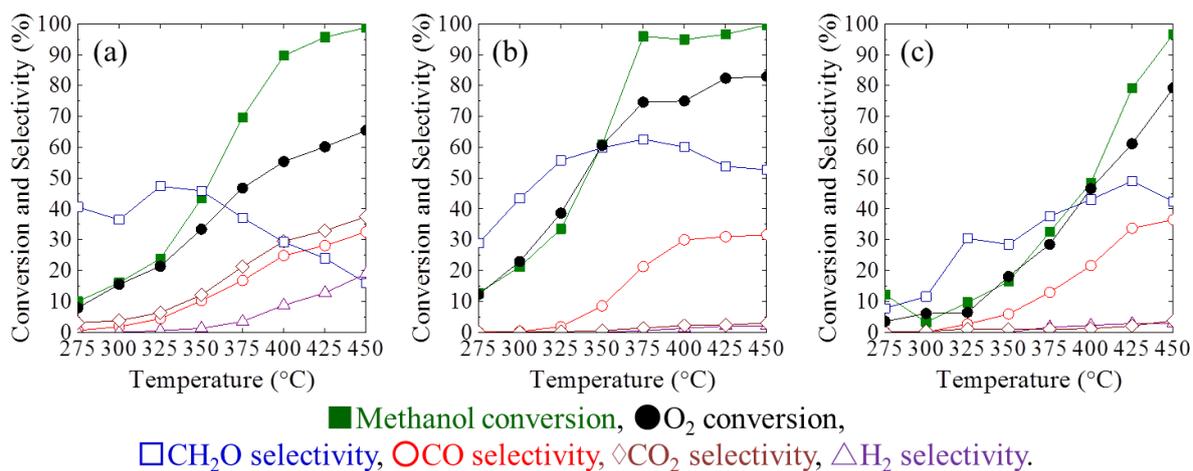
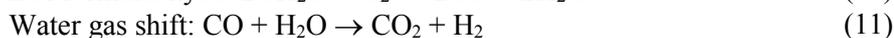
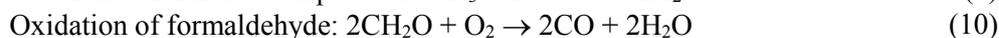


Figure 5. Conversion and selectivity of partial oxidation of methanol over (a) CrO_x/CZ , (b) MoO_x/CZ and (c) WO_x/CZ .

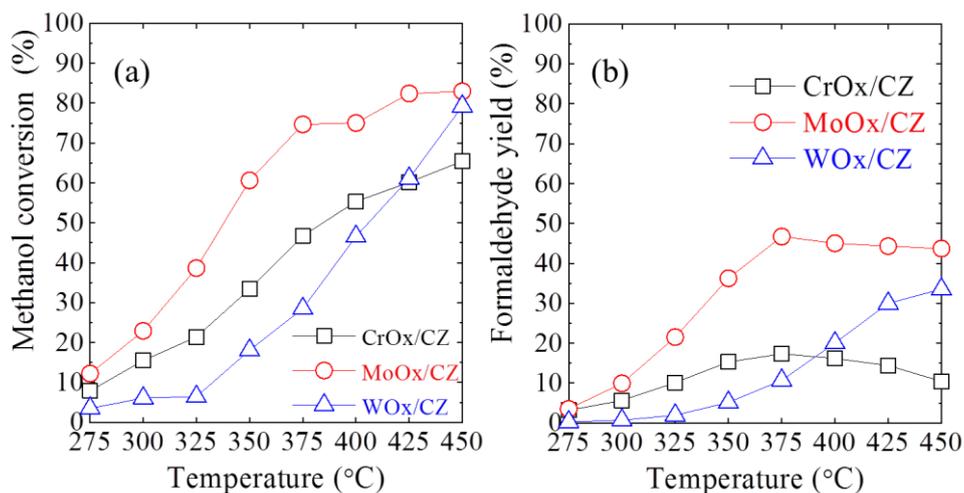


Figure 6. Temperature dependency of (a) methanol conversion and (b) formaldehyde selectivity over catalysts.

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_2O_3 , MoO_3 or WO_3 were successfully synthesized on the support and all these catalysts resulted in the selective formation of formaldehyde (CH_2O). The MoO_3 supported on $\text{CeO}_2\text{-ZrO}_2$ showed the highest methanol conversion and CH_2O yield among these three catalysts.

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