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# Hydrogen production by steam reforming of dimethoxymethane over bifunctional CuO-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

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## ABSTRACT

Dimethoxymethane steam reforming (DMM SR) to a hydrogen-rich gas over bifunctional CuO-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was studied. Complete DMM conversion was observed over 10wt.% CuO-5wt.% ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst under atmospheric pressure, T = 280–300 °C, GHSV = 10000 h<sup>-1</sup> and H<sub>2</sub>O/DMM = 5 mol/mol with hydrogen productivity of ~16.5 L H<sub>2</sub>/(g<sub>cat</sub>·h). Based on the data on the performance of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under DMM SR conditions, the possible role of each catalyst component is discussed.

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## Introduction

In recent years, special attention is concentrated on the development of catalytic steam reforming (SR) process for hydrogen production from synthetic oxygenated organic compounds, such as methanol and dimethyl ether (DME), for polymer electrolyte membrane fuel cells (PEMFC) applications [1–13]. It has been shown that these compounds, in contrast to hydrocarbons, can be steam reformed easily and selectively to hydrogen-rich gas at relatively low temperatures (250–350°C).

Similarly to methanol and DME, dimethoxymethane (DMM) is an easy to synthesize oxygenated compound of C<sub>1</sub>

chemistry. DMM is generally produced by condensation of methanol with formaldehyde. Direct catalytic oxidation of methanol to DMM is under development now [14]. Under normal conditions, DMM is a liquid. Therefore, it can be easily stored and transported. It is worth emphasizing that DMM is a noncorrosive, nontoxic material with a wide scope of applications [15]. It is used as a unique powerful solvent for aerosols, pump sprays in pharmaceutical and perfume industries [16]. DMM selective oxidation is a new alternative for the production of highly concentrated formaldehyde [17]. Direct DMM PEMFCs are being developed now, although they are still less efficient than PEMFC fueled by hydrogen [18]. DMM can be used as an additive to diesel fuel to improve combustion and

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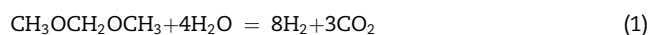
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reduce pollutant emissions of diesel engines [19]. Note again that DMM, in contrast to highly toxic methanol, is an environmentally benign chemical that is of key importance for household and portable fuel cell applications. These facts together with the recent data on DMM SR reported in Refs. [20–24] predict increased DMM demand that will become a promising feedstock for production of hydrogen-rich gas for PEM FC feeding.

Only few papers on DMM SR have been published [20–24]. Overall DMM SR to hydrogen-rich gas is expressed by equation:



It has been shown [20–24] that the reaction proceeds via a consecutive two-step mechanism including DMM hydration to methanol and formaldehyde (2), followed by steam reforming of the formed methanol (3) and formaldehyde (4) to hydrogen-rich gas:



Carbon monoxide can be also formed during DMM SR, for example, by reverse water-gas shift reaction:



In Refs. [20–22], DMM SR to hydrogen-rich gas was performed using mechanically mixed catalytic systems comprised of a solid acid catalyst (niobium phosphate  $\text{NbOPO}_4$ , acid carbon nanofibers H-CNF and acid carbon material derived from carbonization of phenolic resin H-HSPRC) for DMM hydration and a Cu-based catalyst ( $\text{CuZnO}/\text{Al}_2\text{O}_3$  containing (mole %) 63 Cu, 21 Zn and 16 Al) for methanol/formaldehyde SR. The systems showed good performance and, depending on the catalyst compositions, provided for complete DMM conversion and  $\text{H}_2$  productivity of 1.2–7.4 L  $\text{H}_2/(\text{g}_{\text{cat}} \cdot \text{h})$  at 240 °C. However, for mechanically mixed catalysts it is difficult to prepare a uniformly mixed catalyst bed that does not disintegrate into components during reaction. Recently, efficient bifunctional  $\text{CuO}-\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  catalysts have been suggested for DMM SR [23,24]. It was shown that DMM SR on these catalysts proceeds via DMM hydration to methanol and formaldehyde on  $\gamma\text{-Al}_2\text{O}_3$  acid sites and steam reforming of the formed methanol and formaldehyde to hydrogen-rich gas on alumina supported mixed copper–cerium oxide species.

The present work reports the results of studies on DMM SR to hydrogen-rich gas over bifunctional  $\text{CuO}-\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$  catalysts. To elucidate the role of each catalyst component in DMM SR, the data on catalytic performance of  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$  are presented as well. Comparative analysis of available DMM SR data is performed.

## Experimental

5–15 wt.%  $\text{CuO}$ –5 wt.%  $\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$  catalysts were prepared by incipient wetness co-impregnation of  $\gamma\text{-Al}_2\text{O}_3$  ( $S_{\text{BET}} = 200 \text{ m}^2/$

g,  $V_{\text{pore}} = 0.7 \text{ cm}^3/\text{g}$ , granule diameter 0.25–0.5 mm) with aqueous solutions of copper (II) and zinc (II) nitrates (Sigma–Aldrich) taken at the desired ratio. Method of preparation of these catalysts was similar to that described in Ref. [9]. 10 wt.%  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  and 5 wt.%  $\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$  catalyst samples were prepared by incipient wetness impregnation of the  $\gamma\text{-Al}_2\text{O}_3$  with aqueous solution of copper (II) and zinc (II) nitrates respectively. The samples were dried at 100 °C in air and calcined at 400 °C for 3 h in air.  $\gamma\text{-Al}_2\text{O}_3$  was provided by JSC Katalizator, Novosibirsk, Russia, and was calcined at 500 °C for 4 h in air before being used as the support.

Actual  $\text{CuO}$  and  $\text{ZnO}$  loadings in the catalysts were determined by inductively coupled plasma atomic emission spectrometry (Optima instrument; Perkin–Elmer). The specific BET surface areas ( $S_{\text{BET}}$ ) of the support and the catalysts were determined from the nitrogen adsorption isotherms at –196 °C using a TriStar 3000 apparatus.

Table 1 presents  $\text{CuO}$  and  $\text{ZnO}$  loading and  $S_{\text{BET}}$  for the studied catalysts. It can be seen that the calculated (according to preparation protocol)  $\text{CuO}$  and  $\text{ZnO}$  loadings correspond to the actual values obtained by chemical analysis.  $S_{\text{BET}}$  of this catalysts is lower by  $\leq 25\%$  than that of  $\gamma\text{-Al}_2\text{O}_3$  ( $200 \text{ m}^2/\text{g}$ ).

DMM steam reforming was carried out in a U-shaped fixed-bed continuous-flow quartz reactor (i.d. 4 mm) at 150–300 °C under atmospheric pressure. The temperature was measured by means of a chromel/alumel thermocouple inserted into the center of the catalyst bed. All the catalysts (particle size of 0.25–0.5 mm) were pre-reduced *in situ* at 300 °C for 1 h using 5 vol. %  $\text{H}_2$  in  $\text{N}_2$ . Then the reaction temperature was lowered to 150–200 °C in flowing  $\text{H}_2/\text{N}_2$  gas mixture, and the catalysts were exposed to the feed composed of (vol. %) 14 DMM, 70  $\text{H}_2\text{O}$  and 16  $\text{N}_2$ . DMM (gas),  $\text{H}_2\text{O}$  (liquid) and  $\text{N}_2$  (gas) were supplied to an evaporator maintained at 120 °C. Here, water was evaporated and mixed with DMM and  $\text{N}_2$ , and the obtained reaction mixture was fed to the reactor. DMM was introduced to the evaporator by bubbling  $\text{N}_2$  through a glass saturator filled with DMM (99.5 Acros Organics) maintained at 20 °C;  $\text{N}_2$  was fed by a mass-flow controller (Bronkhorst). The liquid water was fed to the evaporator by a plunger pump.

The total GHSV was  $10000 \text{ h}^{-1}$  and WHSV  $\sim 16 \text{ L} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ . The compositions of the inlet and outlet gas mixtures were analyzed by a gas chromatograph (GC Chromos-1000) equipped with TCD/FID detectors and Porapak T/molecular sieve (CaA) columns. Argon was used as a carrier gas. The detection limits for  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , DMM, DME, formaldehyde, methyl formate were  $5 \cdot 10^{-3}$  vol.% or better. The carbon imbalance in all catalytic experiments was below  $\pm 3\%$ .

The DMM conversion ( $X_{\text{DMM}}$ ) and hydrogen productivity ( $W_{\text{H}_2}$ ) were calculated using the following equations:

$$X_{\text{DMM}}(\%) = \frac{C_{\text{DMM}}^{\text{in}} - C_{\text{DMM}}^{\text{out}} \times \frac{C_{\text{N}_2}^{\text{in}}}{C_{\text{N}_2}^{\text{out}}}}{C_{\text{DMM}}^{\text{in}}} \times 100 \quad (6)$$

$$W_{\text{H}_2} \left( \frac{\text{L}}{\text{h} \cdot \text{g}_{\text{cat}}} \right) = \frac{F \times C_{\text{H}_2} \times \frac{C_{\text{N}_2}^{\text{in}}}{C_{\text{N}_2}^{\text{out}}}}{100 \times m_{\text{cat}}} \quad (7)$$

where  $C^{\text{in}}$ ,  $C^{\text{out}}$  are the inlet and outlet concentrations,  $F$  – total flow rate of the inlet reaction mixture (L/h),  $m_{\text{cat}}$  – catalyst weight (g).

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