Performance of bifunctional CuO–CeO$_2$/γ-Al$_2$O$_3$ catalyst in dimethoxymethane steam reforming to hydrogen-rich gas for fuel cell feeding

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ABSTRACT

Dimetoxymethane steam reforming (DMM SR) to hydrogen-rich gas over a bifunctional CuO–CeO$_2$/γ-Al$_2$O$_3$ catalyst was studied. The performance of γ-Al$_2$O$_3$, CeO$_2$/γ-Al$_2$O$_3$, and CuO/γ-Al$_2$O$_3$ under DMM SR conditions was studied as well to elucidate the role of each catalyst component. BET, TPR, FTIR spectroscopy, XRD, TEM, EDXA and HAADF-STEM techniques were used for catalyst characterization. Complete DMM conversion was observed over the CuO–CeO$_2$/γ-Al$_2$O$_3$ catalyst under atmospheric pressure, $T = 300\,°C$, GHSV = 10,000 h^{-1} and H$_2$O/DMM = 5 mol/mol with hydrogen productivity of 15.5 L H$_2$/(g$_{cat}$·h) and CO content in the hydrogen-rich gas below the equilibrium value. DMM SR proceeds via a consecutive two-step reaction mechanism including DMM hydration to methanol and formaldehyde on γ-Al$_2$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 CuO–CeO$_2$/γ-Al$_2$O$_3$ catalyst proved to be highly promising for multi-fuel processor approach: steam reforming of DMM, dimethyl ether and methanol on the same catalyst under similar reaction conditions to hydrogen-rich gas for fuel cell feeding.

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1. Introduction

Power units based on low- and high-temperature (LT and HT) polymer electrolyte membrane fuel cells (PEMFC) are considered as alternative environmentally sound sources of electricity [1–5]. PEMFCs are fuelled by hydrogen, which is usually generated by catalytic steam reforming (SR) of hydrocarbons or oxygenated organic compounds to produce synthesis gas, which is then upgraded to hydrogen-rich gas with low CO content.

Generation of hydrogen-rich gas for PEMFC feed applications from synthetic oxygenated organic compounds, such as methanol and dimethyl ether (DME), attracts attention of scientists for a long time [1–16]. It has been shown that methanol and DME, in contrast to hydrocarbons, can be converted easily and selectively to hydrogen-rich gas at relatively low temperatures (250–350 °C). Efficient methanol and DME SR catalysts have been proposed. They made it possible to design catalytic "fuel processors" – generators of hydrogen-rich gas.

Similarly to methanol and DME, dimethoxymethane (DMM) is an easy to synthesize oxygenated compound of C$_1$ chemistry. DMM is generally produced by condensation of methanol with formaldehyde. Direct catalytic oxidation of methanol to DMM is under development now [17]. 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 [18]. It is used as unique powerful solvent for aerosols, pump sprays in pharmaceutical and perfume industries [19]. DMM selective oxidation is a new alternative for the production of highly concentrated formaldehyde [20]. Direct DMM PEMFCs are being developed now, although they are still less efficient than PEM FC fuelled by hydrogen [21]. DMM can be used as an additive to diesel fuel to improve combustion and reduce pollutant emissions of diesel engines [22]. 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 [23–26] predict increased DMM demand that will become a promising feedstock for production of hydrogen-rich gas for PEM FC feeding.

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Catalytic steam reforming of DMM is one of the most efficient methods for production of hydrogen-rich gas:

$$CH_3OCH_2OCH_3 + 4H_2O = 8H_2 + 3CO_2 \quad (1)$$
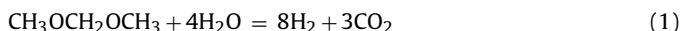
DMM SR studies are still at an early stage. Only several papers have been published [23–26]. It has been shown that the reaction proceeds via a consecutive two-step mechanism including DMM hydration to methanol and formaldehyde (2), followed by steam reforming of the formed methanol (3) and formaldehyde (4) to hydrogen-rich gas:

$$CH_3OCH_2OCH_3 + H_2O = 2CH_3OH + CH_2O \quad (2)$$

$$CH_3OH + H_2O = 3H_2 + CO_2 \quad (3)$$

$$CH_2O + H_2O = 2H_2 + CO_2 \quad (4)$$

Note that the DMM SR reaction mechanism is inherently similar to that of DME SR. According to [10–16], DME SR also proceeds via a consecutive two-step reaction mechanism including DME hydration to methanol, followed by methanol SR to hydrogen-rich gas.

Carbon monoxide can be also formed during DME SR [10–16] and DMM SR [23–26], for example, by reverse water-gas shift reaction:

$$CO_2 + H_2 = CO + H_2O \quad (5)$$

In [23–25] DMM SR was performed using mechanically mixed catalytic systems comprised of a solid acid catalyst for DMM hydration and a Cu-based catalyst for methanol/formaldehyde SR. The systems showed good performance and, depending on the catalyst compositions, provided for complete DMM conversion and H_2 productivity of 1.2–7.4 L H_2/(g_{cat} h) at 250–300 °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 CuO–CeO$_2$/γ-Al$_2$O$_3$ catalysts have been suggested for DMM SR [26]. These catalysts contain both the surface acid sites of γ-Al$_2$O$_3$ for DMM hydration and Cu-based species for methanol/formaldehyde SR. According to [13,14], CuO–CeO$_2$/γ-Al$_2$O$_3$ catalysts are active for methanol and DME SR as well. It was shown that DME hydration proceeds on the acid sites of γ-Al$_2$O$_3$, whereas methanol SR is catalyzed by alumina-supported mixed copper–cerium oxide species CuO–CeO$_2$ (which most likely consist of a solid solution of copper ions in ceria).

The present work reports the results of studies on DMM SR to hydrogen-rich gas over the most efficient bifunctional catalyst 10 wt.% CuO–5 wt.% CeO$_2$/γ-Al$_2$O$_3$. The catalyst was characterized by BET, TPR, XDR, FTIR spectroscopy, TEM, EDXA and HAADF-STEM techniques. To elucidate the role of each catalyst component in DMM SR reaction, the data on the catalytic performance of γ-Al$_2$O$_3$, 5 wt.% CeO$_2$/γ-Al$_2$O$_3$, and 10 wt.% CuO/γ-Al$_2$O$_3$ are presented as well. Based on the data on DME SR and methanol SR over 10 wt.%CuO–5 wt.%CeO$_2$/γ-Al$_2$O$_3$ catalyst the feasibility of developing a multi-fuel processor for generating hydrogen-rich gas from DMM, DME and methanol for PEMFC feeding applications is considered.

2. Experimental

2.1. Catalyst preparation

10 wt.%CuO–5 wt.%CeO$_2$/γ-Al$_2$O$_3$ catalyst sample was prepared by incipient wetness co-impregnation of γ-Al$_2$O$_3$ (S_{BET} = 200 m^2/g, V_{pore} = 0.7 cm^3/g, granule diameter 0.25–0.5 mm) with aqueous solutions of copper (II) and cerium (III) nitrates taken at the desired ratio. 10 wt.%CuO/γ-Al$_2$O$_3$ and 5 wt.%. CeO$_2$/γ-Al$_2$O$_3$ catalyst samples were prepared by incipient wetness impregnation of the γ-Al$_2$O$_3$ with aqueous solutions of copper (II) and cerium

(III) nitrates, respectively. The samples were dried at 100 °C in air and calcined at 400 °C–500 °C for 3 h in air. The catalysts are denoted hereinafter as CuO–CeO$_2$/γ-Al$_2$O$_3$, CuO/γ-Al$_2$O$_3$, and CeO$_2$/γ-Al$_2$O$_3$. γ-Al$_2$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.

2.2. Catalyst characterization

Actual CuO and CeO$_2$ loadings in the catalysts were determined by inductively coupled plasma atomic emission spectrometry (Optima instrument; Perkin-Elmer). The specific BET surface areas (S_{BET}) of the support and the catalysts were determined from the nitrogen adsorption isotherms at −196 °C using a TriStar 3000 apparatus.

Temperature-programmed reduction (TPR) experiments were carried out using a STA 409 PC Luxx derivatograph fitted with a QMS-200 mass spectrometer. The samples (∼50 mg) were heated from room temperature to 400 °C (5 °C/min) in a 5 vol.% H$_2$–Ar mixture flowing at 140 mL/min.

FTIR spectroscopy (Shimadzu FTIR-8300 spectrometer) was applied to determine the acidity of the catalysts by monitoring low-temperature CO adsorption according to the procedure described in [27,28]. The catalysts were reduced and degassed in the IR cell at 400 °C, cooled to −173 °C and treated with doses of CO from 0.1 to 10 torr. The used procedure makes it possible to determine both the amount and strength of Brönsted acid sites (BAS) and Lewis acid sites (LAS), which exhibit adsorption bonds at 2150–2175 cm^{-1} and 2180–2240 cm^{-1}, respectively.

X-ray diffraction (XRD) patterns of the catalysts were recorded on a URD-63 diffractometer (CuK$_\alpha$ radiation; graphite monochromator). The scanning range was 20–80° (2θ) with a step of 0.02° (2θ) and sampling time of 1.0 s. The diffraction data were processed using the PowderCell 2.4 programme yielding the phase composition, lattice parameters, and the size of coherent-scattering regions (CSR) of the samples. Data from the JCPDS international diffraction database were used as a reference.

Transmission electron microscopy (TEM) images and energy-dispersive X-ray (EDX) chemical microanalysis patterns of the catalysts were obtained using a JEM 2010 electron microscope (JEOL, 0.14 nm resolution at 200 kV) coupled with an EDX spectrometer (EDAX Co., Si(Li) detector with 130 eV energy resolution).

The analysis of the surface composition and compositional homogeneity of the supported particles in the catalyst was performed using a high-angle annular dark-field scanning TEM (HAADF-STEM) technique. The photographs and maps were taken on a 200 kV JEOL 2200FS TEM/STEM. The microscope was equipped with a HAADF-detector to obtain images of high atomic contrast in scanning mode, and with an EDX-analyzer for local microanalysis and EDX-local mapping.

2.3. Catalyst testing

DMM, methanol and DME steam reforming reactions were carried out in a *U*-shaped fixed-bed continuous-flow reactor (i.d. 4 mm) at 150–380 °C under atmospheric pressure. 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.% H$_2$ in N$_2$. Then the temperature was lowered to 150–200 °C in flowing H$_2$, and the catalysts were exposed to the feed composed of (vol.%) 14 DMM, 70 H$_2$O and 16 N$_2$ (for DMM SR); 40 methanol, 40 H$_2$O and 20 N$_2$ (for methanol SR) or 20 DME, 60 H$_2$O and 20 N$_2$ (for DME SR). The total gas hourly space velocity (GHSV) was 10,000 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 Porapack T/molecular sieve (CaA) columns. Argon was used as a carrier gas.