Hydrogen generation from oxygenated compounds of C_1 chemistry for Low- and High- Temperature PEM Fuel Cells

Sukhe D. Badmaev[a,b,c]*, **M.V. Konishcheva**[a,b,c], **A.A. Pechenkin**[b,c], **D.I. Potemkin**[a,b,c], **V.D. Belyaev**[b,c], **P.V. Snytnikov**[a,b,c], **V.A. Sobyanin**[b]

[a] *EFCOM LLC, Moscow, Nobel St.5, 143026, Russia*
[b] *Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva 5, Novosibirsk, 630090, Russia*
[c] *Novosibirsk State University, Pirogova St. 2, Novosibirsk, 630090, Russia*

**Corresponding author: sukhe@catalysis.ru*

Abstract:

Production of hydrogen by steam reforming of dimethyl ether, methanol and dimethoxymethane was studied over bifunctional $CuO\text{-}CeO_2/\gamma\text{-}Al_2O_3$ catalyst. It was found that the catalyst provided the hydrogen production rate ~15 l H_2/ (g_{cat} · h) at complete conversion of C1 compound to hydrogen-rich gas with low CO content at 300–350°C. Thus, bifunctional catalyst demonstrates high promises for the realization of multifuel processor concept. It enables the production of hydrogen-rich gas from more than one fuel under similar reaction conditions. Moreover, the produced hydrogen-rich gas can be used for HT PEM FC and, after CO removal for LT PEM FC.

Keywords: hydrogen production, PEM fuel cell, bifunctional catalyst, methanol, dimethyl ether, dimethoxymethane

1. Introduction

At present, fuel cell-based power plants are becoming increasingly common as an alternative and environmentally friendly sources of electrical energy for various applications. They are usually fed by pure hydrogen or hydrogen-rich gas mixtures produced by catalytic conversion of hydrocarbons or oxygenated hydrocarbons. Dimethyl ether (DME), methanol and dimethoxymethane (DMM) are synthetic materials (fuels) which can be easily and selectively converted to hydrogen-rich gas at relatively low temperature (250-350°C) compared to other fuels such as natural gas, gasoline and LPG [1-3].

Overall methanol, DME and DMM steam reforming (SR) are expressed by equations:

$CH_3OH + H_2O = 3H_2 + CO_2$

$CH_3OCH_3 + 3H_2O = 6H_2 + 2CO_2$

$CH_3OCH_2OCH_3 + 4H_2O = 8H_2 + 3CO_2$

It is well known that Cu-containing catalysts are effective for methanol SR [1]. It is generally assumed that DME SR and DMM SR proceed via consecutive two-step reaction mechanism: the first step is hydration of DME/DMM to methanol/formaldehyde over acid sites; the second step is steam reforming of the produced methanol/formaldehyde to hydrogen-rich gas [2,3] .

This work presents the results of the study of the catalytic properties of $CuO\text{-}CeO_2/\gamma\text{-}Al_2O_3$ catalysts with respect to DME SR, methanol SR, DMM SR to hydrogen-rich gas.

2. Experimental

The $CuO\text{-}CeO_2/\gamma\text{-}Al_2O_3$ catalysts were synthesized by treating γ-alumina ($S_{BET} = 200$ m^2/g, $V_{pore} = 0.7$ cm^3/g, granule diameter 0.25–0.5 mm) with solutions of copper and cerium salts taken at the given ratio. The samples were dried at 100°C and calcined at 400°C for 2h. The catalyst was characterized by BET, TPR, XRD, FTIR spectroscopy, TEM, EDXA and HAADF-STEM techniques.

DME, methanol and DMM SR were performed in a fixed bed flow reactor at atmospheric pressure, GHSV=10000 h^{-1}, temperature 150-370°C. The composition of the inlet and outlet gas mixtures were analyzed by GC equipped with TCD/FID and Porapack T/molecular sieve (CaA) columns.

3. Results and discussion

The results obtained prove $CuO-CeO_2/\gamma-Al_2O_3$ to be efficient catalyst for DME, methanol and DMM SR to hydrogen-rich gas with a low CO content. The catalysts were characterized by XRD, HRTEM, EDX and FTIR spectroscopy. Note that the presence of copper oxide, ceria, and alumina is of key importance for getting the active and stable catalysts for DME, methanol and DMM SR. It was shown that catalytic performance of $CuO-CeO_2/\gamma-Al_2O_3$ for DME and DMM SR associated with the $\gamma-Al_2O_3$ acidic centers and with the formation of a copper–cerium mixed oxide, which were responsible for, respectively, DME/DMM hydration and methanol/formaldehyde SR reactions.

To estimate the catalyst feasibility for multi-fuel processor applications (i.e, generation of hydrogen-rich gas from various feed-stocks over the same catalyst under similar reaction conditions), it seemed reasonable to compare its performance in DMM, DME and methanol SR reactions.

Table 1 presents the following: temperature of almost complete conversion of DMM, DME and methanol yielding H_2, CO_2 and CO as the main products; H_2 selectivity; CO concentration in the obtained hydrogen-rich gas; hydrogen productivity. Complete conversion of DMM, DME and methanol was reached at 300, 370 and 300°C respectively. Regardless the feedstock type, the catalyst yielded gas mixtures with low CO content (<1 vol.%). The latter fact is important as it allows using a simpler scheme for production of hydrogen-rich gas for fuel cell application that dictates strict requirements regarding the CO impurity. The hydrogen-rich gas produced by DMM, DME and methanol SR can be used for direct feeding of HT PEM FC without any further CO removal. For LT PEM FC feeding, the hydrogen-rich gas should be purified of CO to the level of 10 ppm, which can be achieved by selective oxidation or methanation of CO.

Table 1. Performance of the $CuO–CeO_2/\gamma-Al_2O_3$ catalyst in DMM, DME and methanol steam reforming to hydrogen-rich gas.

Reaction	Inlet composition, vol.%	T, °C	S_{H_2} %	CO vol.%	W (H_2), l/(h · g_{cat})
DMM SR	$CH_3OCH_2OCH_3:H_2O:N_2$= 14:70:16	300	95	0,5	15.5
DME SR	$CH_3OCH_3:H_2O:N_2$= 20:60:20	370	90	1	15
Methanol SR	$CH_3OH:H_2O:N_2$ = 40:40:20	300	95	1	15

Hydrogen productivity of $CuO-CeO_2/\gamma-Al_2O_3$ (Table 1) in DMM, DME and methanol SR reactions is almost the same and amounts to ~15 L $H_2/g_{cat}\cdot h$. So, 50 g of the catalyst is sufficient to provide operation of a 1 kW PEMFC-based power unit using any substrate – DMM, DME or methanol– as the primary fuel.

References

1. X. Zhang, P. Shi, J. Mol. Catal. A: Chem. 194 (2003) 99-105.
2. A. Pechenkin, S. Badmaev, V. Belyaev, V. Sobyanin, Appl. Catal. B 166-167 (2015) 535-543.
3. Q. Sun, A. Auroux, J. Shen, J. Catal. 244 (2006) 1–9.