Hydrogen production by partial oxidation of dimethyl ether over noble metal catalysts

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Abstract:

Production of hydrogen by partial oxidation (PO) of dimethyl ether (DME) was studied over supported metal (Rh, Ru, Pt) catalysts. It was shown that Pt/CeO_2-ZrO_2, Ru/CeO_2-ZrO_2 and Rh/CeO_2-ZrO_2 catalysts provided complete conversion of DME to hydrogen-rich gas at 500 – 700°C, atmospheric pressure, GHSV = 10000 h^{-1} and DME:O_2:N_2 = 30:15:55 (vol.%).

Keywords: hydrogen production, Rh, Ru, Pt, dimethyl ether, partial oxidation, CeO_2-ZrO_2

1. Introduction

Analysis of current literature [1-3] shows that DME which can be synthesized directly from synthesis gas will play an important role in energy transfer. Thus hydrogen-rich gas produced by PO DME [2,3], seems to be very attractive for fuel cells and other applications.

Overall PO DME is expressed by equation:

$(CH_3)_2O + 0.5O_2 = 2CO + 3H_2$

Studies of PO DME are at the initial stages, and only a few works are available. It is generally assumed that PO DME over supported metal catalysts occurs by the sequential kinetic scheme via the stage of the formation of methane, followed by steam/dry reforming of the formed methane to hydrogen-rich gas.

The present work reports the performance of the Pt/CeO_2-ZrO_2, Ru/CeO_2-ZrO_2 and Rh/CeO_2-ZrO_2 catalysts in PO DME to hydrogen-rich gas to be used for fuel cell feeding.

2. Experimental

The catalysts containing Pt, Ru and Rh deposited on the CeO_2-ZrO_2 (granule diameter 0.25–0.5 mm) in amount of 0.1 μmol/g (1 wt.% Ru and Rh, 1.9 wt.% Pt), denoted further as Ru/CZ, Rh/CZ and Pt/CZ, respectively, were prepared by the method of sorption-hydrolytic deposition. The samples were dried and reduced in hydrogen flow at 250°C for 30 min. The BET specific surface area of the prepared catalysts was close to that of the CZ support 70 $m^2 g^{-1}$. The catalyst was characterized by TPR, TPO, XRD, TEM, EDXA and HAADF-STEM techniques.

PO DME was performed in a fixed bed flow quartz reactor at atmospheric pressure, temperature 300 – 700 ^oC, GHSV=10000 h^{-1}, DME:O_2:N_2 = 30:15:55 (vol.%). 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

Fig. 1 illustrates the effect of temperature on the outlet product concentrations in PO DME over the Ru/CZ, Rh/CZ and Pt/CZ catalysts. It is worthwhile to note that only H_2, CO, CO_2, CH_4 and H_2O were detected among the reaction product. Fig. 1 shows also the temperature dependencies of respective calculated equilibrium values.

As shown in Fig. 1, temperature dependencies of the outlet product concentrations were the same for all catalysts. The outlet product concentrations were close to the respective equilibrium values at 500 – 600 ^{o}C. Also the conversion of DME increased with temperature and was close to the respective equilibrium value up to 500^{o}C (not shown in figure).

The results obtained prove Ru/CZ, Rh/CZ and Pt/CZ to be efficient catalysts for PO DME to hydrogen-rich gas. For instance, the Pt/CZ catalyst provided the hydrogen productivity and yield of ~6 L $H_2/(g_{cat}\cdot h)$ and ~ 80%, respectively, under experimental conditions: T = 700 °C, P = 1 atm, and GHSV = 10000 h^{-1} for DME:O_2:N_2 = 30:15:55 (vol.%). Besides, the catalyst showed good stability at 650 – 700 ^{o}C.

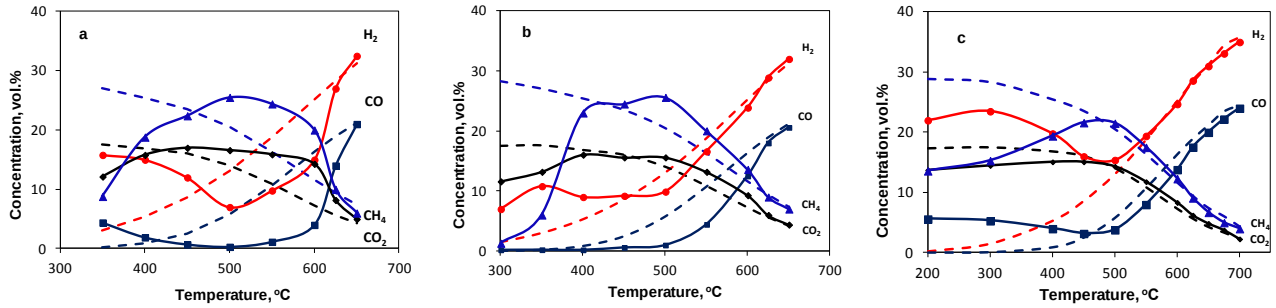

Fig. 1. Effect of temperature on the outlet product concentrations in PO DME over Ph/CZ (a), Ru/CZ (b) and Rt/CZ (c) catalysts. Solid lines – experiments, dotted lines – thermodynamic equilibrium values.

References

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