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Hydrogen Production from Methanol Steam Reforming over Cu/ZnO/Al₂O₃/CeO₂/ZrO₂ Nanocatalyst in an Adiabatic Fixed-Bed Reactor

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Abstract: Hydrogen production from steam reforming of methanol is performed in an adiabatic fixed bed heterogeneous reactor by using Cu/ZnO/Al₂O₃/CeO₂/ZrO₂ nanocatalyst. The catalyst was prepared by co-precipitation method and characterized by TGA, XRD, SEM and BET. By changing the mean average temperature of the catalyst bed (or reactor operation temperature) from 230 to 270°C, variations in methanol conversion were monitored. The results showed that the conversion of methanol was strongly dependent on the reaction temperature. In addition, the effects of weight hourly space velocity (WHSV) on methanol conversion were investigated. According to the results, the maximum conversion was obtained at 270°C with WHSV of 15 h⁻¹.

Key words: Hydrogen production · Methanol steam reforming · Co-precipitation · Nanocatalyst · Fixed-bed reactor

INTRODUCTION

Catalytic steam reforming of methanol is a well-established process used for the production of hydrogen [1–4]. This process is especially important for polymer electrolyte fuel-cells, which generate electrical power by electrochemical oxidation of hydrogen with atmospheric oxygen [5]. The use of methanol as an on-board hydrogen source is attractive for fuel-cell engines in transportation applications because of its safe handling, low cost and ease of synthesis from a variety of feed stocks (biomass, coal and natural gas) [6]. Moreover, methanol has been recommended as the best source for hydrogen fuel among the high energy density liquid fuels, due to the high H/C ratio having a lower propensity for soot formation than other hydrocarbons, relatively low boiling point and easy storing [7].

Hydrogen production systems via steam reforming of methanol (SRM) constitute a promising technology for energy feeding in portable electronic devices, for decentralized refueling units for hydrogen-based automobiles or as on-board generation systems for hydrogen-based internal combustion engines or PEM fuel cells [5].

There are three process alternatives for the conversion of methanol to hydrogen [8]:

- Decomposition,
- Steam reforming,
- Partial oxidation.

The decomposition reaction is a strong endothermic reaction:

$$CH_3OH \leftrightarrow CO + 2H_2 \quad \Delta H_0 = 128 \text{ kJ/mol} \qquad (1)$$
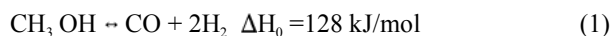
The process yields high CO contents, which makes the process unsuitable for fuel cell applications. The steam reforming process, Eq. (2), is also endothermic; however it yields CO₂ as the major by-product and
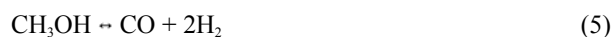

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can produce a high H_2 content, up to 75% on a dry basis, which makes it very favorable for fuel cell applications:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad \Delta H_0 = 131 \text{ kJ/mol} \qquad (2)$$
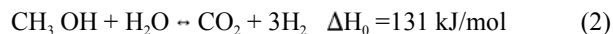
Partial oxidation, Eq. (3), is a strong exothermic reaction, which can yield an automotive system with a fast response compared to the steam reforming reaction. However, the system can only iver 66% hydrogen when pure oxygen is used and as low as 41% when air is supplied instead of oxygen, which is the realistic alternative in an automotive system [8-15]:

$$CH_3OH + \frac{1}{2}O_2 \leftrightarrow CO_2 + 2H_2 \quad \Delta H_0 = -155 \text{ kJ/mol}$$
$$(3)$$
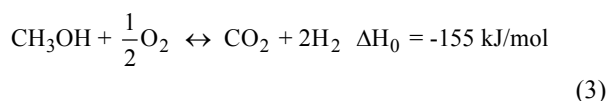
The steam reforming of methanol for production of H_2 from CH_3OH involves three reactions:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \qquad (4)$$

$$CH_3OH \leftrightarrow CO + 2H_2 \qquad (5)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (6)$$

These are the steam reforming reaction (4), the methanol decomposition reaction (5) and the water gas shift reaction (6). Reaction (4) is the preferred pathway of H_2 production and reaction (6) plus the reverse of reaction (5) should be suppressed to prevent CO formation. The platinum anode in the PEM fuel cell gathering is sensitive to CO poisoning at concentrations as low as 10 ppm, so the aim is to produce CO-free H_2 to the greatest extent possible [8, 16]. The major advantage of SRM over MD (methanol decomposition) and POM (partial oxidation of methanol) is the high H_2 selectivity, which makes it favorable for fuel cell applications [17, 18].

In the literature, copper-based catalysts have received considerable attention for production of H_2 by SRM [19-21]. To improve the efficiency of catalysts of the SRM reaction, several researchers have introduced a third metallic oxide, ZrO_2, into CuO/ ZnO/Al_2O_3 catalysts. The promoting effect of ZrO_2 has been attributed to the improvement in reducibility [22-24]. It is reported that addition of ZrO_2 improves the specific surface area, Cu surface area and Cu dispersion of catalyst and prevents the sintering of Cu, improving the activity and stability of the catalyst [25]. Likewise, CeO_2 has also been applied

to increase the Cu dispersion and the thermal stability of the catalysts and even to reduce the CO concentration [26-28].

In this work, $Cu/ZnO/Al_2O_3/CeO_2/ZrO_2$ nanocatalyst was prepared by co-precipitation method and used for the steam reforming of methanol in an adiabatic fixed bed reactor. Methanol conversion and the catalyst bed temperature changes in a laboratory-scale system at various operating temperatures and various WHSVs were investigated.

Experimental

Catalyst Preparation: The oxide precursors $Cu/ZnO/Al_2O_3/CeO_2/ZrO_2$ with approximate composition of (weight ratio) Cu/Zn/Al/Ce/Zr: 40/50/5/2.5/2.5 was prepared by the conventional co-precipitation method. A mixed aqueous solution of copper nitrate 3-hydrate $(Cu(NO_3)_2.3H_2O)$, zinc nitrate 3-hydrate $(ZnO(NO_3)_2.3H_2O)$, zirconium nitrate 8-hydrate $(Zr(NO_3)_2.8H_2O)$, aluminum nitrate 9-hydrate $(Al(NO_3)_3.9H_2O)$, cerium nitrate 3-hydrate $(Ce(NO_3)_2.3H_2O)$ (each 1 M) and a solution of sodium carbonate (1 M) were added slowly and simultaneously into 300 mL of deionized water at 65°C with vigorous stirring. The pH was kept constant at 7. The precipitates were aged in mother liquid for 3.5 h at the same temperature under stirring, washed with deionized water to remove Na^+ and NO^{-3} in the filtrate and then dried at 383 K for 13 h and calcined by air at 623 K for 4 h (heating rate 5°C min^{-1}). Each calcined catalyst was pelletized in a hydraulic press, crushed and sieved into a particle size of 0.45-0.5 mm and used as catalyst for steam reforming of methanol reaction.

Catalyst Characterization: The proper temperature of the calcination process of the dried samples was determined by means of a thermo gravimetric analyzer using Diamond TG/DTA instrument (PerkinElmer, USA). In order to avoid any diffusion effect and formation of thermal gradients, the amount of the used samples were ranged from 10 to 15 mg. The catalyst samples were heated from 25 up to 550°C at 1 °C/min with air flow rate of 200 ml/min, till no weight loss occurred. X-ray diffraction (XRD) patterns for the oxide particles were obtained on a Bruker D8 instrument with monochromatic Cu Ka radiation (λ=1.5406 Å) operated at 40 kV and 30 mA, scanning 2θ from 20 to 80. The specific surface area, pore size distribution and pore volume of the sample was measured using the Brunauer-Emmett-Teller (BET) method by nitrogen adsorption using a BEL SORP-max instrument (BEL, JAPAN). Prior to adsorption measurements,
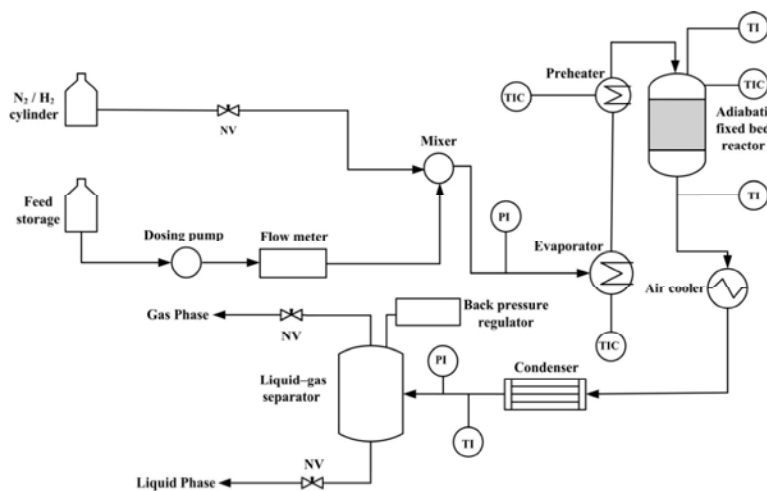
Fig. 1: A schematic diagram of the experimental apparatus for catalytic production of H_2 from methanol
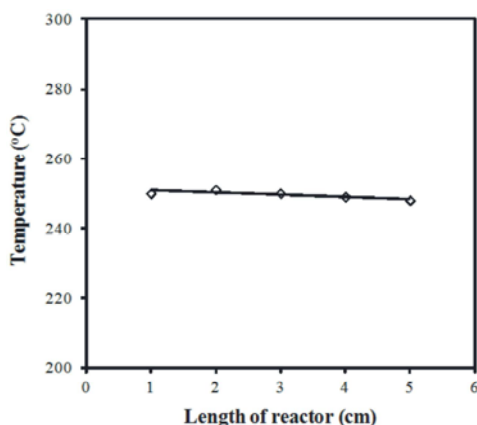

Fig. 2: Temperature profile inside the reactor in a blank experiment (without any reaction)

the samples were degassed for at least 5 h at 300°C. Scanning electron microscopy (SEM) was performed in a XL30 (Philips, Poland) microscope, operated at 15 kV.

Experimental Setup: The schematic diagram of the employed set up is shown in Fig. 1. Catalytic tests were performed in a fixed-bed continuous flow reactor with 5 cm height operated under atmospheric pressure. Before each run, the catalysts were pre-reduced in a stream of 10% H_2/N_2 (500 mL/min) at the normal pressure according the following heating program: heated from room temperature to 300°C with heating rate 10°C/min and was kept for at the stated temperature for 2 hours. The molar ratio of $H_2O:CH_3OH$ in the feed was 1.3:1. Water and methanol mixture was pumped from storage tank at different rates from 200 mLh^{-1} up to 400 mLh^{-1} to an evaporator and then to a supper heater before entering the reactor. The superheated methanol was sent to an

adiabatic fixed-bed reactor. The axial reactor temperature at any point of the catalyst bed was measurable via a thermo-well using a thermocouple. The reactor outlet products were passed through an air cooler and a double pipe heat exchanger to cool down to the ambient temperature. The cooled products were sent to a gas-liquid separator. A back pressure regulator (BP-LF690, pressure Tech 2000, England) was placed on the separator to regulate the system pressure. Gaseous reaction product was sent to gas chromatograph analyzer (GC) (Varian CP-3800) for online measurement using TCD and FID detectors by packed column (HYSEP Q, Custom made, Iran) and capillary column (CP-Sil 8 CB, Varian, USA). Also, the remaining methanol in the exit product was measured and the methanol conversion was calculated with respect to entrance methanol.

To confirm the adiabatic operation of the applied reactor used, an experiment was performed as a blank run (without any reaction) and the temperature across the reactor bed was measured using thermocouple and thermowell. The result of this experiment is shown in Fig. 2. According to the illustrated data, it is reasonable to assume that the reactor behaves adiabatic reactor. This experiment was performed by passing air through the catalyst bed.

RESULT AND DISCUSSION

Thermal Analysis: Fig. 3 shows the TG/DTA plot of a synthesized sample (Cu/ZnO/Al$_2$O$_3$/CeO$_2$/ZrO$_2$) prepared by co-precipitation method. This figure shows that pre-catalytic exothermic reaction causes catalyst weight reduction to about 76% of its initial dried weight. This catalyst has a weight lost between 25-100°C due to
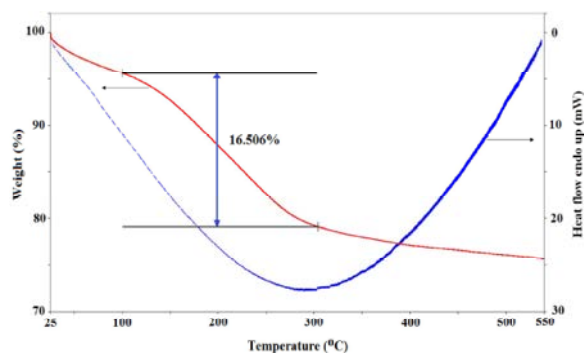
Fig. 3: XRD patterns of Cu/ZnO/Al$_2$O$_3$/CeO$_2$/ZrO$_2$ catalyst after calcination

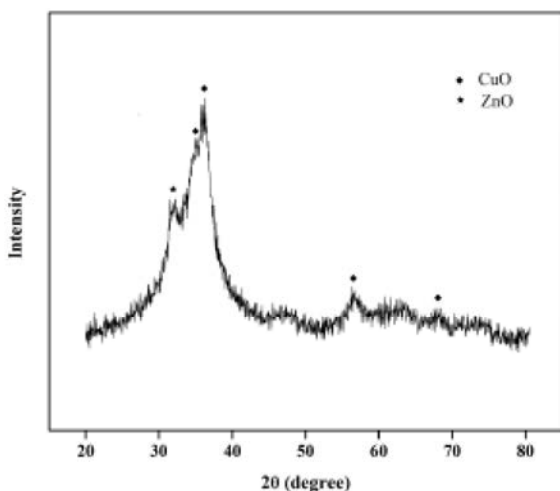Fig. 5: SEM image of the Cu/ZnO/Al$_2$O$_3$/CeO$_2$/ZrO$_2$ catalyst

Fig. 4: XRD patterns of catalyst prepared with co-precipitation method after calcination

desorption of humidity and crystallized water on the surface and structure of the catalyst. The major mass reduction appeared at temperatures between 100-304°C that is due to release and evaporation of volatile compounds as well as conversion of metal compounds formed during co-precipitation to stable metallic oxides. In addition, as shown in the TGA graph, there is a small mass reduction at temperatures above 300°C verifying the residues of additional volatile compounds being completely removed and the catalyst reached to stable structure.

The DTA curve presents one major peak at 300°C that is exothermic resulting from the elimination of humidity and volatile compounds. Higher temperatures (above 400°C) resulted in sintering of Cu-base particles which contributed to reduction of fine pores, hence, decrease in active surface area. The dried deposition of Cu/ZnO/Al$_2$O$_3$ catalysts is often calcined for 3 to 10 hours at a temperature between 250-350°C to achieve
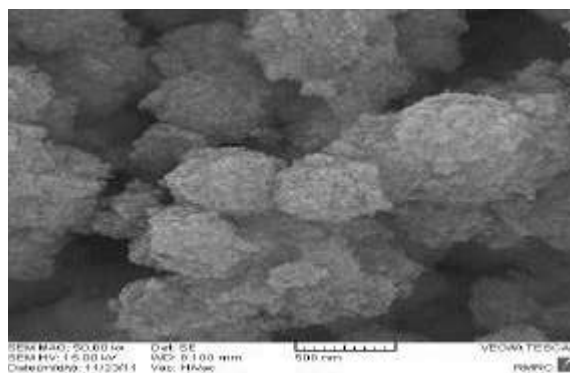
heterogeneous catalyst [29, 30]. TGA/DTA analysis showed that when the temperature is set at 350 °C, almost 87% of the catalyst is calcined and sintering of copper particles is avoided.

Phase analysis: The XRD pattern of the synthesized Cu/ZnO/Al$_2$O$_3$/CeO$_2$/ZrO$_2$ sample with co-precipitation method is shown in Fig. 4. This figure indicates that the sample calcined at 350°C, has a crystallite CuO phase. The crystalline structure is a characteristic that is strongly dependent on the condition of calcination catalyst construction method. The average crystallite size was calculated using Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{7}$$

where k is a constant ~0.9, λ is the wavelength of the X-ray, β is the full width of diffraction peak at half maximum intensity (FWHM) and θ is the diffracting angle.

Morphology: Fig. 5 shows the SEM images of the prepared catalyst by co-precipitation method in an aqueous medium after calcinations. According to this figure, the crystals of the sample have good dispersion and the morphology of these crystals is almost regular. This result confirms the crystalline particle size obtained by XRD analysis.

Bet and Pore Size Distribution Analysis: Physical properties of the selected catalysts (specific surface area, total pore volume and average pore diameter) are presented in Table 1. The average crystallite size was calculated using Scherrer equation and was estimated to be about 5.63 nm.

Table 1: Physical properties of Cu/ZnO/Al$_2$O$_3$/CeO$_2$/ZrO$_2$ catalyst

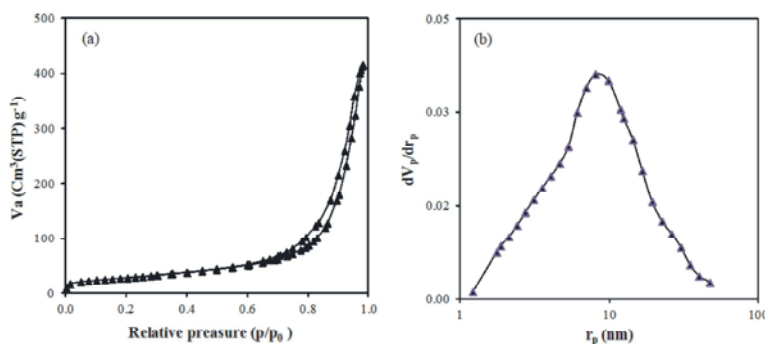| Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)	crystallite size (nm)[a]
137	0.7603	22.046	5.63

[a]determinate by XRD results

Fig. 6: (a) N$_2$ adsorption/desorption isotherm and (b) pore size distribution of the sample
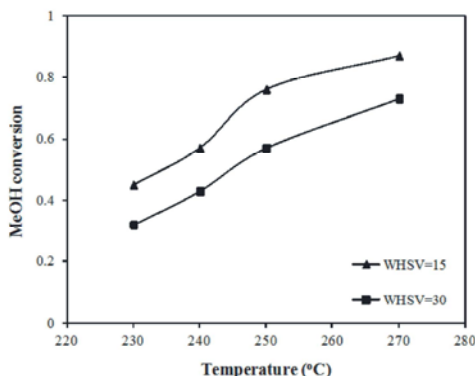

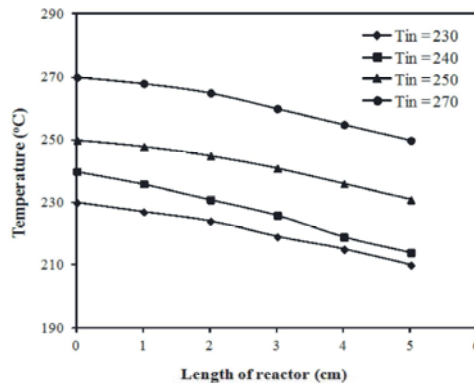
Fig. 7: Methanol conversion versus inlet feed temperature

Fig. 9: Temperature profile along the catalyst bed at various inlet feed temperatures and WHSV = 30 h^{-1}. Solid lines show the trend of these variations
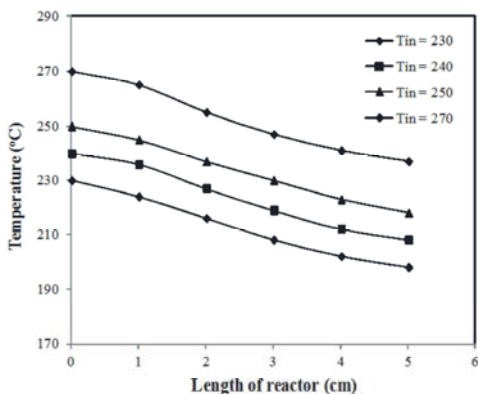

Fig. 8: Temperature profile along the catalyst bed at various inlet feed temperatures and WHSV = 15 h^{-1}. Solid lines show the trend of these variations
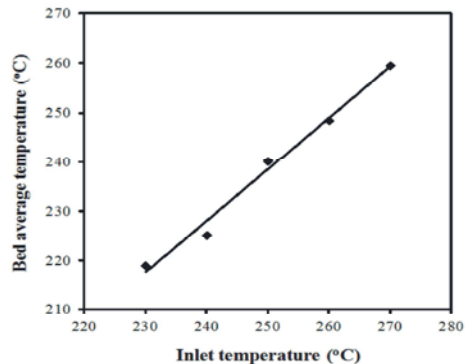

Fig. 10: Catalyst bed average temperature (operating temperature) versus inlet feed temperature. Solid symbols are experimental data and solid line shows the trend of changes

The pore size distributions and N$_2$ adsorption/desorption isotherm of the sample are shown in Fig. 6. The nitrogen adsorption/desorption isotherms can be classified as a type VI isotherm, typical of mesoporous materials. According to IUPAC classification, the hysterics loop is type H$_1$ occurs at a relative pressure range (p/p$_0$ = 0.7–0.9), indicating

a broad pore size distribution with uniform size and shape.

Catalytic Reaction: The obtained experimental data are shown in Figs. 7-10. In Figs. 8 and 9 variations of temperature versus reactor length for different WHSVs are presented.

The Temperature Effect: The first series of experiments were conducted to investigate the effect of operating temperature of the reactor on methanol conversion. According to Fig. 6, it can be observed that conversion of methanol was increased by increasing the inlet feed temperature. Since the reaction is endothermic and the reactor was adiabatic, the temperature of catalyst bed decreased from the feed inlet temperature, as illustrated in Figs. 8 and 9.

The change in catalyst bed average temperature (reactor operating temperature) versus inlet feed temperature is shown in Fig. 10. According to this Figure, there seems to be a relatively linear correlation between the change in the reactor operating temperature and the feed inlet temperature.

Effect of Whsv on Methanol Conversion: The influence of WHSV on the conversion of methanol at four different inlet feed temperatures (230-270°C) is also shown in Figs. 7 and 8. At a constant inlet temperature, methanol conversion increases with decreasing WHSV. Increasing the WHSV will cause an increase in the gas velocity, which promotes mass transfer but leads to a decrease in the contact time of reactant species. As a result, the conversion of methanol increases with decreasing WHSV.

CONCLUSIONS

A Cu/ZnO/Al$_2$O$_3$ nanocatalyst was prepared by co-precipitation method, modified by adding small amounts of Zr and Ce oxides. This catalyst was used for the production of hydrogen by methanol steam reforming in an adiabatic packed bed reactor at different inlet feed temperatures ranging from 230 to 270 °C. The influence of WHSV on the conversion of methanol and bed temperature was investigated. The results showed that the methanol conversion increased with decreasing WHSV and the temperature of catalyst bed decreased from the feed inlet temperature along the adiabatic reactor.

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