Catalysis Letters Vol. 103, Nos. 3–4, October 2005 (© 2005)
DOI: 10.1007/s10562-005-7160-8

Study of partial oxidative steam reforming of methanol over Cu–ZnO/samaria-doped ceria catalyst

Jenshi B. Wang[a], Chia-Hao Li[b], and Ta-Jen Huang[b,]*

[a]*Department of Chemical Engineering, I-Shou University, Kaohsiung, Taiwan 840, ROC*
[b]*Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 300, ROC*

Received 6 April 2005; accepted 10 June 2005

Partial oxidative steaming reforming of methanol (POSRM) to produce hydrogen selectively for polymer electrolyte membrane fuel cell (PEMFC) powering vehicles was studied over Cu–ZnO/samaria-doped ceria (SDC) catalyst. Compared with Cu–ZnO/α-Al_2O_3 and Cu–ZnO/γ-Al_2O_3 catalysts, the Cu–ZnO/SDC catalyst exhibited higher activity for CH_3OH conversion and higher selectivity for H_2 production in the POSRM reaction. The higher catalytic performance of Cu–ZnO/SDC appears attributable to the support effect of SDC. Effects of reaction temperature, O_2/CH_3OH and H_2O/CH_3OH molar ratios on the catalytic performance of Cu–ZnO/SDC were investigated. It has been found that the partial-oxidation nature of the POSRM reaction is increased when O_2/CH_3OH ratio is increased, and the combustion of methanol and H_2 would occur insignificantly in the POSRM over the Cu–ZnO/SDC catalyst. A higher concentration of steam is beneficial to suppress CO formation over the Cu–ZnO/SDC catalyst. Under the experimental conditions of the present work, the O_2/CH_3OH and H_2O/CH_3OH molar ratios should be about 0.02 and 1.0–2.0, respectively, in order for Cu–ZnO/SDC to achieve an optimum catalytic performance.

KEY WORDS: partial oxidative steam reforming; methanol; samaria-doped ceria; Cu–ZnO catalyst.

1. Introduction

Issues of increasingly stringent environmental regulations, declining reserve of fossil fuels, and worsening global warming have provided strong incentives to develop clean electric power sources for vehicles. Currently, hydrogen fueled polymer electrolyte membrane fuel cell (H_2-PEMFC) appears as the most viable technology for powering vehicles. To overcome the difficulties of hydrogen distribution and storage as well as limited driving range with the use of pressurized hydrogen tanks on vehicles for H_2-PEMFC used in mobile applications, it is more feasible for H_2 to be produced on-board from liquid fuels [1,2].

Among various high energy density liquid fuels, methanol remains prominent because of its low cost and conversion temperature, high hydrogen to carbon ratio, and no C–C bond thereby lessening soot formation. For automotive fuel-cell applications, hydrogen can be extracted from methanol through two process alternatives: (i) steam reforming of methanol (SRM), and (ii) partial oxidation of methanol (POM). Although both SRM and POM are effective in generating hydrogen, each has its inherent drawbacks. An alternative method, known as oxidative steam reforming of methanol (OSRM), is to combine SRM and POM by feeding methanol, steam and oxygen concurrently to the reformer to produce hydrogen for PEMFC. In OSRM, the heat needed by the endothermic SRM is supplied by the exothermic POM reaction so that the overall reaction is nearly thermal-neutral, depending on the ratio of the three reactants chosen. As a result, the OSRM process allows the development of a compact hydrogen generator system, particularly suitable for vehicle applications. In addition, through OSRM it is possible to obtain a more dynamic process allowing for rapid reformer startup, as well as circumventing one of the main drawbacks of POM of forming hot spots in the catalyst bed.

Despite the benefits of OSRM, there have been significantly fewer studies of this reaction compared with a spate of works on SRM. The addition of oxygen to the SRM reaction over Cu–ZnO and Cu–ZnO/γ-Al_2O_3 catalysts was initially investigated by Huang and co-workers [3,4,5] who demonstrated that 30–40 wt% Cu was the most active for the POM/SRM reactions. Kumar *et al.* [6] in a preliminary report showed that, among several different metals and supports for OSRM, the catalyst $CuO/ZnO/Al_2O_3$ exhibited high activity and selectivity for H_2 production. Murcia-Mascaros *et al.* [7] recently studied the OSRM reaction over CuZnAl catalysts derived from hydrotalcite-like precursors and found that high activity of methanol conversion and very high selectivity of H_2 could be obtained. Moreover, Velu *et al.* [8,9] reported that CuZnZr-oxide catalysts are more effective for the OSRM reaction than CuZnAl oxides due to improved Cu reducibility, higher Cu metal surface area, and dispersion imparted by the oxygen

---

* To whom correspondence should be addressed.
E-mail: tjhuang@che.nthu.edu.tw

vacancies of zirconia. In line with this, it appears of interest to study Cu–Zn catalysts over different supports for this reaction.

Oxygen-ion conducting oxides such as ceria, when used as supports, are known to significantly impart metal-support interaction to enhance catalytic performances, due to their easy formation of oxygen vacancies [10,11], improved dispersion of metals [12,13], and excellent capabilities of oxygen storage/transport [12, 13]. Doped ceria has been the subject of considerable interests because the addition of dopants greatly increases the concentration of oxygen vacancies [14], or improves thermal stability of ceria [15]. Samaria is one of the best possible dopants to modify structural and chemical properties of ceria because the ionic radius and electronegativity of samarium are close to those of cerium [16]. Although the importance of oxygen-ion conducting oxides as catalyst supports and the resulting support effect to upgrade catalysts in many reactions have been recognized, there have been very few investigations [17,18] concerning the use of ceria as support, particularly of samaria-doped ceria (SDC), in the study of SRM or OSRM.

In this work, the performance of Cu–ZnO/SDC in 'partial' oxidative (substantially sub-stoichiometric O_2 concentration) steam reforming of methanol (POSRM) is investigated comparing with the results of Cu–ZnO/α-Al_2O_3 and Cu–ZnO/γ-Al_2O_3 conventional catalysts. Effects of operating variables such as reaction temperature, O_2/CH_3OH and H_2O/CH_3OH molar ratios on the catalytic performance of Cu–ZnO/SDC are elucidated in order to gain more insight into the reaction.

2. Experimental

2.1. Catalyst preparation and characterization

SDC was prepared from reagent-grade (99.9% purity, Strem Chemical) metal nitrates $Sm(NO_3)_3\cdot 6H_2O$ and $Ce(NO_3)_3\cdot 6H_2O$ by a co-precipitation method. Appropriate amounts of samarium nitrate and cerium nitrate corresponding to an atomic molar ratio of Sm:Ce = 1:9 were dissolved in deionized water to make solutions. Hydrolysis of the metal salts to hydroxides was achieved by slowly dropping such solution into NH_4OH solution, and, in the meantime, stirring to keep the pH of the solution >10. A distinct deeply purple color of precipitate/gel was formed when the nitrate solution was dropped into NH_4OH. A centrifuge was employed to isolate the gel, which was then washed twice by deionized water, and once by ethanol. After washing, the gel was dried under vacuum at 100 °C for 4 h, ground, and then calcined in air at 300 °C for 2 h and at 500 °C for 4 h. Afterwards, the prepared SDC was slowly cooled down to room temperature.

The Cu–ZnO/α-Al_2O_3, Cu–ZnO/γ-Al_2O_3 and Cu–ZnO/SDC catalysts with a composition of Cu:Zn:support = 3:3:4 were prepared by co-precipitation of appropriate amount of copper nitrate and zinc nitrate on the supports. A Cu content of 30 wt% was chosen because earlier studies [3,4, 19] have demonstrated that a Cu-Zn catalyst containing 30–40 wt% of Cu was the most active for the POM or SRM reactions. Powders of α-Al_2O_3, γ-Al_2O_3 (99.9%, High Purity Chemicals Institute, Japan) and the above-prepared SDC were first dispersed in de-ionized water at 70 °C. Aqueous solution of $Zn(NO_3)_2\cdot 6H_2O$ (99.0% purity, Showa, Japan) was then slowly dropped for 2 h, followed by drop-wise addition of $Cu(NO_3)_2\cdot 3H_2O$ (99.0% purity, Showa, Japan) solution for another 2 h; while during each drop-wise addition of the nitrate solution, pH of the resulting solution was adjusted by 1 M of NaOH to 7. The resulting crude catalysts were then vacuum-filtered and washed by de-ionized water. After evaporating excess water, the catalysts were dried under vacuum at 105 °C for 12 h, and then calcined in air at 400 °C for 4 h. The calcinations of SDC and catalysts were conducted by passing air at a rate of 1 L/min and by ramping temperature at a rate of 10 °C/min from room temperature.

The BET surface area of the catalysts was determined by means of nitrogen physisorption, applying a thermal conductivity detector instrument (Quantachrome, U.S.A.).

2.2. Activity tests

The activity tests of the catalysts were conducted under atmospheric pressure in a continuous flow reactor charged with 200 mg of catalyst, which was fixed by quartz wool and quartz sand downstream of the bed. The reactor was made of an 8-mm-ID quartz U-tube imbedded in an insulated electric furnace, equipped with a temperature programmable controller to isothermally control the reaction temperature. A K-type thermocouple was inserted into the catalyst bed to measure and control bed temperature. The catalyst sample was initially reduced at 300 °C for 12 h in flowing hydrogen at 100 mL/min to remove possible impurities and to reduce metal oxides to metallic phases. After pre-reduction, the catalyst was slowly cooled down to the reaction temperature of 200–275 °C.

A stream of premixed methanol and water with different molar ratios was fed into a vaporizer by means of a syringe pump (Sage Instruments, 341A) at a liquid flow rate of 2.8 mL/h, vaporized at 110 °C (vaporized flow rate, 100 mL/min), and then carried into the catalyst bed by flowing helium. For conducting partial oxidative steam reforming, O_2 of 1 or 5% of the vaporized methanol and water solution, i.e., O_2 at a flow rate of 1 or 5 mL/min, was then added to the reacting stream of methanol solution 10 min after the steam reforming had been started. After 3 h of operation, the reactor outflow was analyzed on-line by a gas chromatograph (China Chromatography 8900) equipped with a thermal conductivity detector, in series with a CO-NDIR (Beckman 880) and an O_2 analyzer (Beckman 755A). The GC is installed with Porapak Q plus molecular sieve 5A columns in series at 110 °C using helium as carrier gas to separate H_2, O_2, H_2O and CH_3OH, but with poor separation of CO and CO_2. The CO-NDIR (detection limit, 100 ppm) was able to detect CO from CO_2.

3. Results and discussion

3.1. Performance of catalysts

Figure 1 compares the catalytic activities of α-Al_2O_3–, γ-Al_2O_3– and SDC-supported Cu–ZnO catalysts in partial oxidative steaming reforming of methanol (POSRM) over the temperature range studied. It can be seen that Cu–ZnO/γ-Al_2O_3 and Cu–ZnO/SDC catalysts are active for the POSRM reaction, showing that the resulting methanol conversion and H_2 production rates are moderately influenced by reaction temperature. It is also clearly observable from figure 1 that the effect of catalyst dispersion on the activities of catalysts is quite significant. The Cu–ZnO/γ-Al_2O_3 catalyst exhibits far better catalytic performance in POSRM than Cu–ZnO/α-Al_2O_3, obviously attributed to its higher surface area than that of the latter as referring to the BET areas of these catalysts listed in Table 1. Noting that the catalyst composition is Cu:Zn:support = 3:3:4 and thus

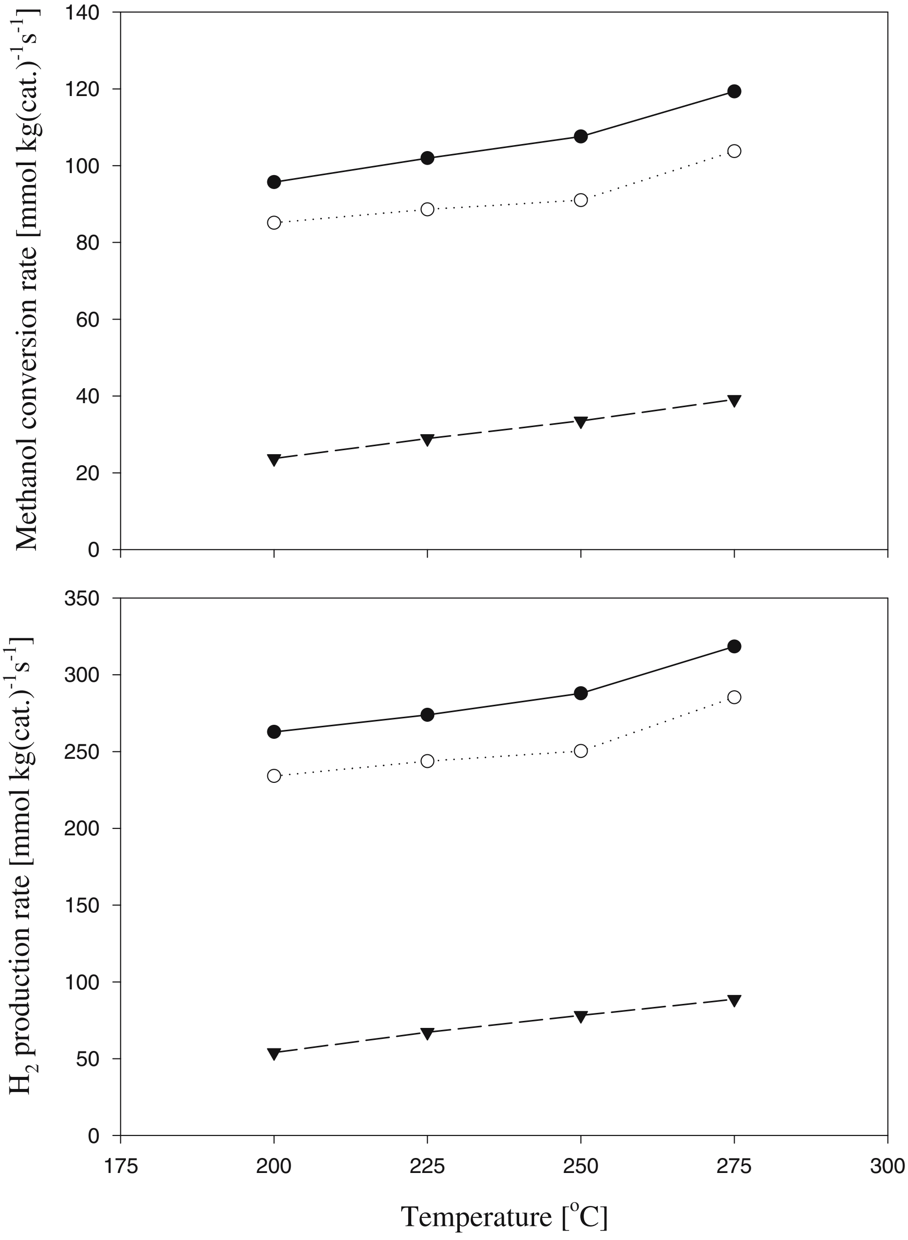

Figure 1. Variations of methanol conversion and H_2 production rates with temperature over (●) Cu–ZnO/SDC, (○) Cu–ZnO/γ-Al_2O_3, and (▼) Cu–ZnO/α-Al_2O_3 catalysts in POSRM reaction for O_2/CH_3OH = 0.075 and H_2O/CH_3OH = 0.5 in molar ratio.

Table 1
BET area, CH_3OH conversion rate, and ratio of CH_3OH conversion rate of Cu–ZnO/SDC to that of pseudo Cu–ZnO/Al_2O_3 in POSRM reaction for O_2/CH_3OH = 0.075 and H_2O/CH_3OH = 0.5 in molar ratio

	BET, m^2/g	CH_3OH conversion rate (mmole/kg-s)			
		200 °C	225 °C	250 °C	275 °C
Cu–ZnO/SDC	25.2	95.7	101.9	107.6	119.3
Cu–ZnO/γ-Al_2O_3	128	85.1	88.6	91.0	103.7
Cu–ZnO/α-Al_2O_3	6.4	23.7	28.9	33.5	39.1
Pseudo Cu–Zno/Al_2O_3	25.2	33.2	38.1	42.4	49.1
		Ratio of CH_3OH conversion rates			
Cu–ZnO/SDC to Pseudo Cu–Zno/Al_2O_3		2.89	2.68	2.54	2.43

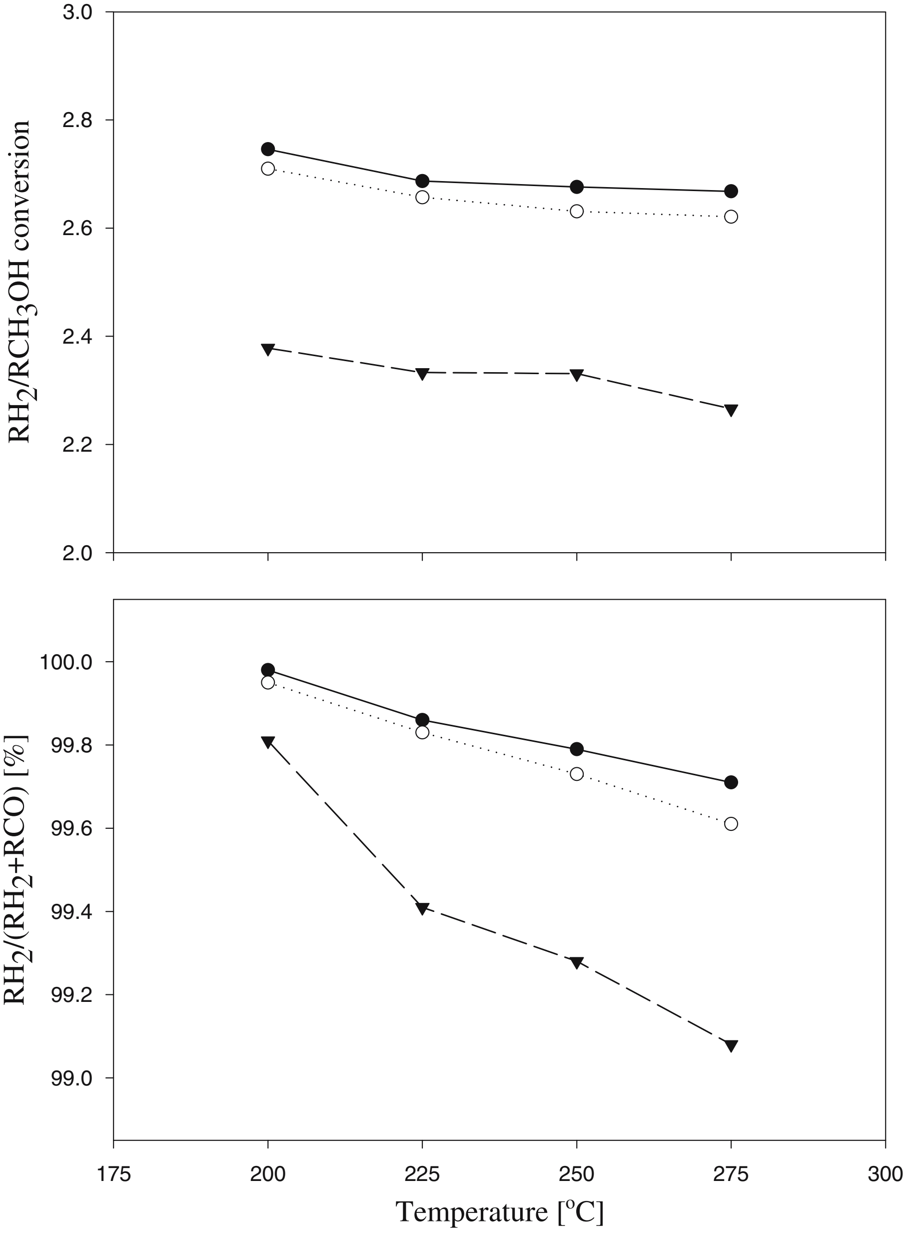

Figure 2. Variations of RH_2/RCH_3OH conversion ratio and selectivity with temperature over (●) Cu–ZnO/SDC, (○) Cu–ZnO/γ-Al_2O_3, and (▼) Cu–ZnO/α-Al_2O_3 catalysts in POSRM reaction for O_2/CH_3OH = 0.075 and H_2O/CH_3OH = 0.5 in molar ratio.

the BET area is a good representation of the available surface area of the catalyst. In addition, although the Cu–ZnO/SDC catalyst has much smaller BET area than that of Cu–ZnO/γ-Al_2O_3, it exhibits the highest methanol conversion and H_2 production rates over these temperatures.

The remarkable catalytic performance of Cu–ZnO/SDC in POSRM can be seen from Table 1 by comparing its methanol conversion rate with that of pseudo Cu–ZnO/Al_2O_3, arbitrarily assuming a BET area of 25.2 m^2/g same as that of Cu–ZnO/SDC. The methanol conversion rate of pseudo Cu–ZnO/Al_2O_3 is obtained by interpolating the corresponding rates of Cu–ZnO/γ-Al_2O_3 and Cu–ZnO/α-Al_2O_3 at their respective BET areas. As a result, as shown in figure 2, Cu–ZnO/SDC arrives at the highest ratio of the rate of H_2 production to the rate of CH_3OH conversion, hereafter referred to as 'RH_2/RCH_3OH conversion', throughout the temperature range of this study. It should be noted that, the higher the RH_2/RCH_3OH conversion is, the higher is the efficiency of the catalyst in POSRM.

The higher catalytic performance of Cu–ZnO/SDC may be attributed to the existence of metal-support interactions due to the formation of interfacial active centers between copper oxide and the oxygen vacancies of ceria in SDC, thereby enhancing the dispersion and hence the catalytic activities of the supported copper particles [20–22]. Similar results in OSRM were reported recently over CuZn–Zr catalysts by Velu and co-workers who ascribed the catalytic synergy between CuZn and ZrO_2 to the unique feature of the latter known to possess oxygen vacancies [23,24].

As also shown in figure 2, Cu–ZnO/SDC can attain the highest H_2 selectivity, defined as the ratio of the rate of H_2 production to that of (H_2 + CO) production. It signifies that more H_2 and less CO can be produced by Cu–ZnO/SDC, and the discrepancy of H_2 selectivity between the catalysts is widening with increasing reaction temperature. Accordingly, these observations may lead to the suggestion that, despite of the complexity of the mechanism of POSRM, the water-gas shift (WGS) reaction of CO may have taken place simultaneously with the reaction of POSRM and have played a more significant role in Cu–ZnO/SDC to produce H_2 than the other two catalysts. This role becomes more pronounced with increasing reaction temperature.

In this study, the O_2/CH_3OH ratio was chosen to be substantially below stoichiometry, since it has been known that the loss of methanol and H_2 by combustion, i.e., $CH_3OH + 1.5\,O_2 \rightarrow CO_2 + 2\,H_2O$ and $H_2 + 0.5\,O_2 \rightarrow H_2O$, is significant at the stoichiometric condition of POM ($O_2/CH_3OH = 0.5$) [19,25]. Figure 3 shows

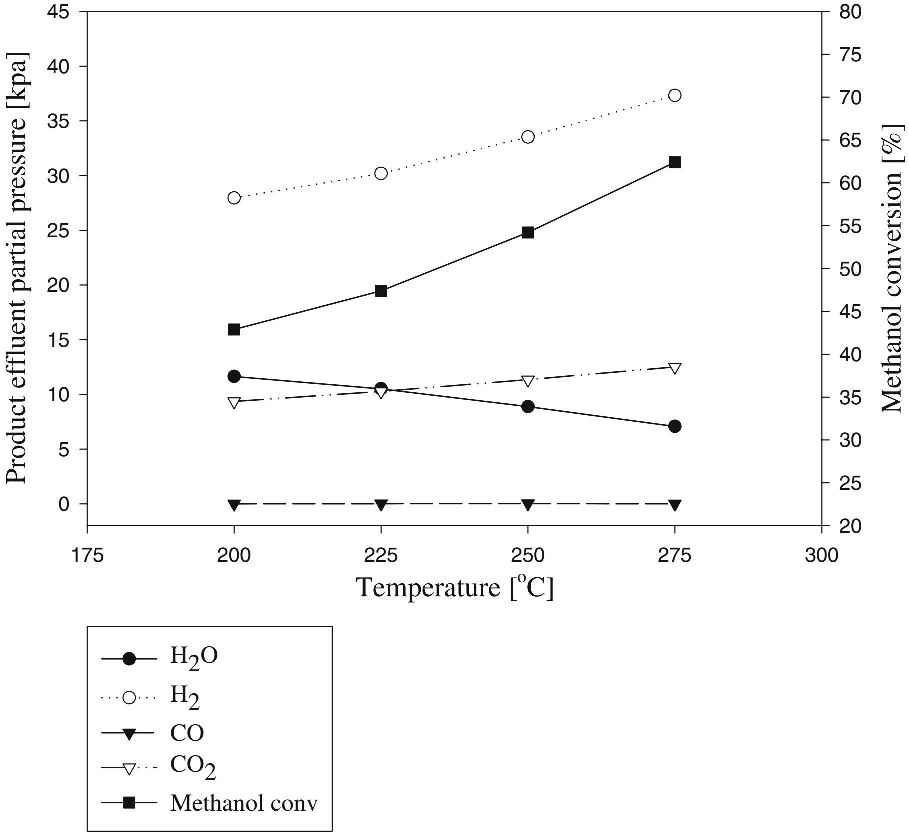

Figure 3. Variations of product effluent partial pressures and methanol conversion with temperature over Cu–ZnO/SDC for $O_2/CH_3OH = 0.02$ and $H_2O/CH_3OH = 1$.

typical results of a sub-stoichiometric-O_2 POSRM reaction versus reaction temperature over the Cu–ZnO/SDC catalyst by keeping the H_2O/CH_3OH molar ratio at 1.0 and O_2/CH_3OH ratio at 0.02. With the O_2 pressure maintained below stoichiometry, the methanol conversions can still reach about 43% at 200 °C and 62% at 275 °C. In contrast to SRM and POM, water is both a reactant and a product in POSRM reactions where, at differential O_2 conversions, water can be produced by combustion of methanol. However, it can be seen clearly from figure 3 that the water content decreases and the H_2 partial pressure increases with increasing reaction temperature throughout the temperature range studied. This reveals that, at this sub-stoichiometric O_2 concentration, only negligible amount of water is produced over the Cu–ZnO/SDC catalyst via combustion of methanol and H_2 at these temperatures.

3.2. *Effect of O_2/CH_3OH molar ratio*

For a POSRM reaction, the concentration of O_2 is expected to have a strong effect on the activities of catalysts since this reaction involves both POM and SRM reactions. Figure 4 presents the effects of O_2/

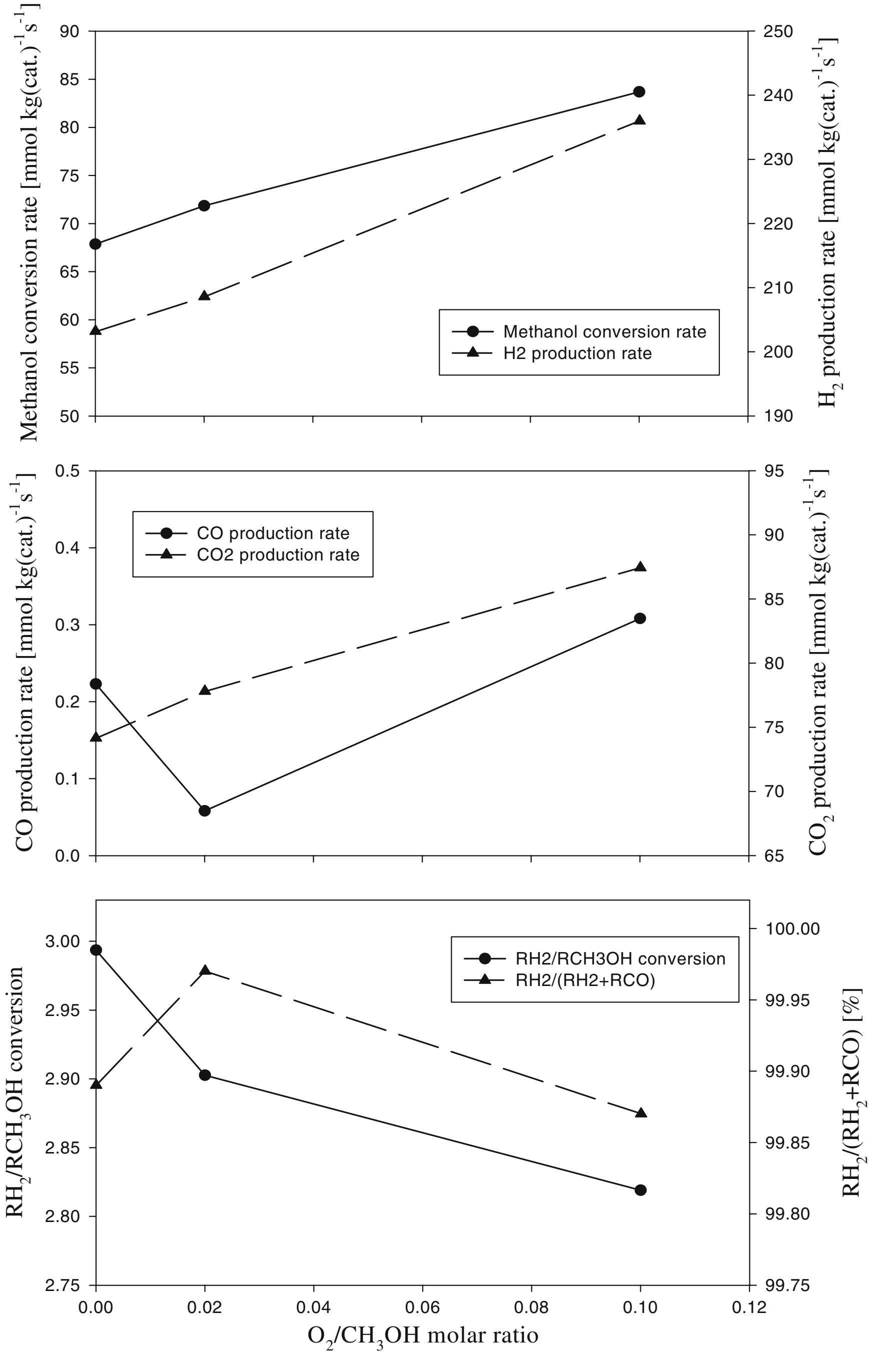

Figure 4. Effect of O_2/CH_3OH molar ratio on the catalytic performance of Cu–Zno/SDC in POSRM at 250 °C and H_2O/CH_3OH = 1.

CH_3OH molar ratio on the catalytic performance of Cu–ZnO/SDC in POSRM at 250 °C with the H_2O/CH_3OH molar ratio fixed at 1. These results indicate that the rates of methanol conversion and the rates of H_2 and CO_2 formation increase with increasing O_2/CH_3OH ratio. The CO production rate declines first and then increases with the increase of O_2/CH_3OH ratio. It implies that, at low O_2 concentrations, CO produced in the POSRM reaction is readily oxidized to CO_2. This can be verified by examining the slope of the rate of CO_2 production in this figure which clearly shows that this slope is steeper for the O_2/CH_3OH ratio ranging from 0 to 0.02 than from 0.02 to 0.1. While at the concentrations of O_2 higher than 0.02, the POM reaction may become relatively more dominant when excess O_2 is involved, thereby resulting in progressive increase of CO formation. The above results can be substantiated by the observation that the RH_2/RCH_3OH conversion ratio decreases with increasing O_2/CH_3OH ratio. This rate ratio is around 3 in the absence of O_2, and is sharply decreasing to 2.90 and then gradually to 2.82 with increasing the O_2/CH_3OH ratio to 0.02 and 0.1, respectively. Note that theoretically the RH_2/RCH_3OH conversion ratio should be 3 for SRM reaction, while it should be 2 in the case of POM reaction. The results of the RH_2/RCH_3OH rate ratio clearly demonstrate that the POM nature of the POSRM reaction is increased when O_2/CH_3OH ratio is increased.

For the Cu–ZnO/SDC catalyst in this work, it is worth noting also that the decrease of the RH_2/RCH_3OH conversion ratio with increasing O_2/CH_3OH ratio is primarily due to the increase of POM nature, with insignificant contribution by the combustion of H_2. This can be verified by the effluent gas compositions of methanol, H_2O and H_2 shown in Table 2, which clearly shows that only very little H_2 was combusted to produce H_2O in the POSRM reaction with $O_2/CH_3OH = 0.02$. In the case of POSRM with $O_2/CH_3OH = 0.1$, the amount of H_2O in the effluent is only slightly higher than that of the unconverted methanol remained in the reactor outflow, indicating that only a slight amount of H_2 was involved in the secondary oxidation. Though insignificant, the secondary H_2 oxidation increases with reaction temperature and oxygen concentration in the feed. Because of the POM nature increases with increasing O_2/CH_3OH ratio during the POSRM reaction, as Table 2 shows, the amount of CO_2 produced increases with reaction temperature and oxygen concentration in the feed. As a consequence, based on the above discussions of the effect of O_2/CH_3OH molar ratio and the result of H_2 selectivity shown in figure 4, it is suggested that the O_2/CH_3OH ratio should be maintained at around 0.02 (i.e., feeding O_2 at 1% of the vaporized methanol solution) in order to achieve an optimum catalytic performance.

3.3. *Effect of H_2O/CH_3OH molar ratio*

Since, as discussed above, the water-gas shifting of CO is more prominent over Cu–ZnO/SDC than the other two catalysts, it is of interest to study the effect of H_2O/CH_3OH molar ratio on the catalytic performance of Cu–ZnO/SDC in POSRM. This study was carried out at 250 °C by feeding O_2 at 1% of the vaporized methanol solution, with the results shown in figure 5. Stoichiometrically, a H_2O/CH_3OH ratio of 0.94–0.97 will be required in POSRM involving the O_2/CH_3OH ratio of 0.015–0.03 for the O_2 feeding rate of 1%. It can be seen from figure 5 that this catalyst exhibits the highest rates of methanol conversion as well as H_2 and CO_2 productions around the H_2O/CH_3OH ratio of 1.0. This reveals that the POM mechanism prevails in this POSRM reaction for the H_2O/CH_3OH ratio up to around 1.0. For the H_2O/CH_3OH ratio ranging between 1.0 and 2.0, the rate of methanol conversion decreases less significantly than that of H_2 production, thereby resulting in progressive increases of RH_2/RCH_3OH conversion ratio; in the mean time, the CO production declines progressively and ultimately becomes undetectable at $H_2O/CH_3OH = 2.0$ and thus H_2 selectivity increases progressively, as shown in figure 5. These results suggest that a higher concentration of steam is beneficial to the reduction of CO, possibly due to water-gas shifting of the latter. As a result, under experimental conditions of the present study, a H_2O/CH_3OH ratio higher than 1.0 can provide a better catalytic performance in terms of

Table 2

Effluent gas compositions, and converted CH_3OH and H_2O, in mmole/kg-sec, vs. reaction temperature during POSRM reaction, with various O_2/CH_3OH ratios, over the Cu–Zno/SDC catalyst for $H_2O/CH_3OH = 1$

	Temp(°C)	CH_3OH		H_2O		H_2	CO_2
		Effl.	conv'td	Effl.	conv'td	Effl.	Effl.
$O_2/CH_3OH = 0.02$	200	75.74	56.85	75.76	56.83	165.6	60.91
	225	69.85	62.74	69.90	62.69	182.2	65.31
	250	60.75	71.84	60.94	71.65	208.5	74.78
	275	49.87	82.72	50.17	82.42	240.2	85.73
$O_2/CH_3OH = 0.1$	200	64.64	67.95	64.70	67.89	192.7	70.30
	225	59.08	73.51	59.37	73.22	208.4	76.50
	250	48.91	83.68	49.24	83.35	235.9	86.40
	275	38.44	94.15	38.80	93.79	265.2	97.11

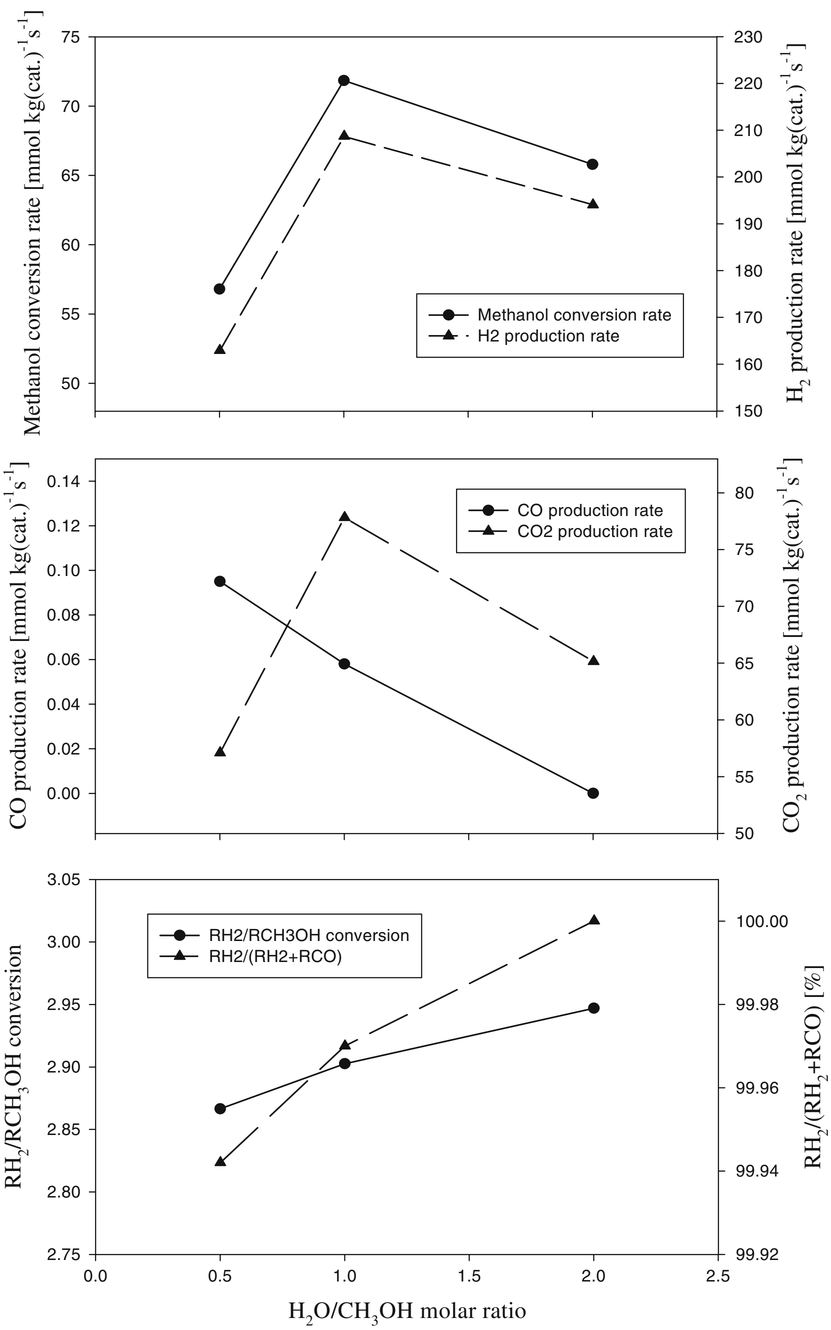

Figure 5. Effect of H_2O/CH_3OH molar ratio on the catalytic performance of Cu–ZnO/SDC in POSRM at 250°C and $O_2 = 1\%$ of the vaporized methanol solution.

RH_2/RCH_3OH conversion ratio, H_2 selectivity and CO production rate. Thus, for practical applications, an excess of steam is beneficial for the Cu–ZnO/SDC catalyst to induce the WGS reaction so as to suppress CO formation.

4. Conclusions

Based on the results obtained in this work, one can conclude that, compared with Cu–ZnO/γ-Al_2O_3 and Cu–ZnO/α-Al_2O_3, the Cu–ZnO/SDC catalyst is more active and efficient for selective production of hydrogen by POSRM. The higher catalytic performance of Cu–ZnO/SDC can be attributed to the metal-support interaction inherently existing between copper and the oxygen vacancies of SDC. The effects of reaction temperature, O_2/CH_3OH and H_2O/CH_3OH molar ratios on the catalytic performance over Cu–ZnO/SDC have been studied. It has been found that the POM nature of the POSRM reaction is increased when O_2/CH_3OH ratio is increased, and combustion of methanol and H_2 would occur insignificantly in the POSRM over Cu–ZnO/SDC under the experimental conditions of this work. A higher concentration of steam is beneficial to suppress the CO formation over the Cu–ZnO/SDC catalyst. Under the experimental conditions of the present work, the O_2/CH_3OH and H_2O/CH_3OH molar ratios of about 0.02 and 1.0–2.0, respectively, are advisable in order to achieve an optimum catalytic performance over the Cu–ZnO/SDC catalyst.

References

[1] P.J. de Wild and M.J.F.M. Verhaak, Catal. Today 60 (2000) 3.
[2] R.A. Lemons, J. Power Sources 29 (1990) 251.
[3] T.J. Huang and S.W. Wang, Appl. Catal. 24 (1986) 287.
[4] T.J. Huang and S.L. Chren, Appl. Catal. 40 (1988) 43.
[5] T.J. Huang and C.L. Cheng, Proc. Third ROK/ROC Joint Workshop on Catalysis, Daejeon, Korea, 1985, p. 80.
[6] R. Kumar, S. Ahmed, M. Krumpelt and K.M. Myles, Argonne National Laboratory Report, ANL-92/31, Argonne, IL, USA, 1992.
[7] S. Murcia-Mascaros, R.M. Navarro, L. Gomez-Sainero, U. Costantino, M. Nocchetti and J.L.G. Fierro, J. Catal. 198 (2001) 338.
[8] S. Velu, K. Suzuki and T. Osaki, Chem. Commun. (1999) 2341.
[9] S. Velu, K. Suzuki, M. Okazaki, M.P. Kapoor, T. Osaki and F. Ohashi, J. Catal. 194 (2000) 373.
[10] J.L.G. Fierro, J. Soria, J. Sanz and J.M. Rojo, J. Solid State Chem. 66 (1987) 154.
[11] E. Abi-Aad, R. Bechara, J. Grimblot and A. Aboukais, Chem. Mater. 5 (1993) 793.
[12] H.C. Yao and Y.F. Yu Yao, J. Catal. 86 (1984) 254.
[13] J.C. Summers and S.A. Ausen, J. Catal. 58 (1979) 131.
[14] C.B. Choudhary, H.S. Maiti and E.C. Subbarao, in: Solid Electrolytes and Their Applications, E.C. Subbarao (ed.), (Plenum Press, New York, 1980, p. 47).
[15] J.E. Kubsh, J.S. Rieck and N.D. Spencer, in: Catalysis and Automotive Pollution Control II, A. Crucq (ed.), (Elsevier, Amsterdam, 1991, p. 125).
[16] T.H. Etsell and S.N. Flengas, Chem. Rev. 70 (1970) 339.
[17] Y. Liu, T. Hayakawa, K. Suzuki and S. Hamakawa, Catal. Commun. 2 (2001) 195.
[18] J. Papavasiliou, G. Avgouropoulos and T. Ioannides, Catal. Commun. 5 (2004) 231.
[19] L. Alejo, R. Lago, M.A. Pena and J.L.G. Fierro, Appl. Catal. A 162 (1997) 281.
[20] J.B. Wang, W.-H. Shih and T.J. Huang, Appl. Catal. A 203 (2000) 191.
[21] J.B. Wang, D.H. Tsai and T.J. Huang, J. Catal. 2008 (2002) 370.
[22] J.B. Wang, S.C. Lin and T.J. Huang, Appl. Catal. A 232 (2002) 107.
[23] S. Velu, K. Suzuki, M.P. Kapoor, F. Ohashi and T. Osaki, Appl. Catal. A 213 (2001) 47–63.
[24] S. Velu and K. Suzuki, Top. Catal. 22 (2003) 235.
[25] J. Agrell, K. Hasselbo, K. Jansson, S.G. Jaras and M. Boutonnet, Appl. Catal. A 211 (2001) 239.