ELSEVIER

Catalysis Today 77 (2002) 89–98

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Influence of preparation method on performance of Cu/Zn-based catalysts for low-temperature steam reforming and oxidative steam reforming of methanol for H_2 production for fuel cells

Jian-Ping Shen, Chunshan Song*

Clean Fuels and Catalysis Program, The Energy Institute, Department of Energy and Geo-Environmental Engineering,
The Pennsylvania State University, 209 Academic Projects Building, University Park, PA 16802, USA

Abstract

Several methods (impregnation, co-precipitation and hydrothermal synthesis) have been comparatively examined for the preparation of precursors to Cu/Zn/Al catalysts. Steam reforming and oxidative steam reforming of methanol was performed using the laboratory-prepared and a commercial Cu/Zn/Al catalysts at a relatively low temperature (230 °C) for catalytic production of H_2. The results show that the preparation method significantly affects the catalyst performance with respect to methanol conversion, H_2 yield and CO concentration. The catalyst with lower copper-reduction temperature shows higher activity for methanol conversion at lower temperature. The best Cu/Zn/Al catalyst has been prepared by a co-precipitation method, which shows high activity for methanol conversion (99–100%) and H_2 production (71–76%) with very low CO concentration (0.05–0.15%) in steam reforming (H_2O/methanol = 1.43 mol ratio) and in oxidative steam reforming (O_2/methanol = 0.158–0.474 mol ratio) at a low temperature (230 °C).

Keywords: Fuel cell; Low-temperature steam reforming; Cu/Zn/Al catalyst; Methanol; Copper oxide reduction

---

1. Introduction

Development of fuel cell systems including fuel reformer has attracted increasing attention worldwide in the past several years due to their higher efficiency, environmental advantages and potential market [1]. As an electrochemical device converting chemical energy directly into electricity, fuel cell system can be made and used in various sizes, in principle, according to the power demand. They are highly energy efficient (not limited by Carnot cycle as in traditional internal combustion engine), quiet (involving few moving parts), and more environmentally friendly (very low or zero pollution, with CO_2 and water as the final products). Of the five basic types of fuel cells, proton exchange membrane fuel cell (PEMFC) is one of the most promising fuel cells, which consumes hydrogen and oxygen to produce electricity.

Most studies on hydrogen production for fuel cells are based on two types of carbon compounds: one is oxygen-containing compound, such as alcohol (methanol, ethanol, etc.) and ether (dimethylether, etc.), another involves hydrocarbons such as natural gas, propane gas, gasoline, jet fuel and diesel fuel. The production of hydrogen from alcohol like methanol has received attention due to several advantages as compared to hydrocarbons: reaction conditions are mild due to low ΔH and there are no needs for

---

* Corresponding author. Tel.: +1-814-863-4466;
fax: +1-814-865-3248.
E-mail address: csong@psu.edu (C. Song).

PII: S0920-5861(02)00235-3

desulfurization, pre-reforming, and multiple steps for CO removal. The disadvantages of methanol include the lower energy density and lack of distribution infrastructure as compared to hydrocarbon fuels. The studies on production of hydrogen from methanol involve one or more of the following aspects: (a) methanol decomposition [2,3]; (b) catalytic partial oxidation [4–8]; (c) steam reforming [9–12]; (d) oxidative steam reforming [13–15]; (e) water-gas shift (WGS); and (f) selective CO oxidation, as shown below:

$$CH_3OH = CO + 2\,H_2, \quad \Delta H^\circ = +92.0\,\text{kJ/mol} \qquad \text{(a)}$$

$$CH_3OH + 0.5\,O_2 = CO_2 + 2\,H_2, \quad \Delta H^\circ = -192.2\,\text{kJ/mol} \qquad \text{(b1)}$$

$$CH_3OH + 0.25\,O_2 = 0.5\,CO_2 + 0.5\,CO + 2\,H_2, \quad \Delta H^\circ = -50.8\,\text{kJ/mol} \qquad \text{(b2)}$$

$$CH_3OH + H_2O = CO_2 = 3\,H_2, \quad \Delta H^\circ = +49.7\,\text{kJ/mol} \qquad \text{(c)}$$

$$CH_3OH + 0.25\,O_2 + 0.5\,H_2O = CO_2 + 2.5\,H_2, \quad \Delta H^\circ = -71.4\,\text{kJ/mol} \qquad \text{(d)}$$

$$CO + H_2O = CO_2 + H_2, \quad \Delta H^\circ = -41\,\text{kJ/mol} \qquad \text{(e)}$$

$$CO + 0.5\,O_2 = CO_2, \quad \Delta H^\circ = -283.0\,\text{kJ/mol} \qquad \text{(f)}$$

$$CO_2 + H_2 = CO + H_2O, \quad \Delta H^\circ = +41\,\text{kJ/mol} \qquad \text{(g)}$$

The most promising processes for hydrogen production from methanol for fuel cell applications are steam reforming and oxidative steam reforming in terms of higher hydrogen yield and lower CO concentration. However, current methanol reforming catalyst still produces relatively high concentration of CO (usually 1.0–5.0%) in the products, which is still much higher than the upper limit of CO concentration in feed gas for PEM fuel cells. The presence of CO (>15 ppm) in the gas mixture fed to fuel cell stack will deteriorate the anode catalyst and lower the system efficiency of PEM fuel cells.

CO formation during methanol conversion mainly comes from the following reactions: (i) methanol decomposition (Eq. (a)); (ii) methanol partial oxidation (Eq. (b2)) and (iii) reverse water-gas shift (WGS) reaction (Eq. (g)). During methanol reforming (steam or oxidative steam), these reactions can take place to different extents, depending on the feed compositions, reaction conditions and the nature of the catalyst for reforming. One way to reduce CO formation in the products is the use of a lower reaction temperature, which can suppress the occurrence of methanol decomposition and favor WGS reaction due to the thermodynamic nature of such reactions. It should be kept in mind, however, that methanol steam reforming is more favorable at higher temperature due to the endothermic nature of steam reforming reaction (Eq. (c)). Therefore, in terms of the efficiency of fuel cell system, especially for portable fuel cell, the integrated catalyst system with suitable functions that promote both steam reforming and water gas shift at lower temperatures should be developed.

The effective non-precious metal catalyst for methanol reforming is Cu/Zn-based catalyst. Several research groups [4,5,9,14] reported that methanol conversion over Cu/Zn-based catalysts greatly depends on the status of copper, such as the dispersion, metal surface area and particle size. Catalyst with high copper dispersion shows better performance in methanol steam reforming. The status of metal dispersion should be closely related to overall surface area. Unfortunately, Cu/Zn-based catalysts appear to have low surface area by conventional preparation methods. It is known that the method of preparation plays an important role in the catalytic performance of methanol synthesis catalyst that is also Cu/Zn-based [16]. Thus, in this work we attempted to prepare Cu/Zn/Al catalyst with high surface area by exploring different methods including precipitation and hydrothermal synthesis. A comparative examination of these catalysts was carried out for methanol steam reforming, and then the catalyst performance was correlated with copper reduction properties.

2. Experimental

2.1. Decomposition of copper nitrates

To compare CuO reduction behavior of different precursors, the copper oxide was obtained through direct decomposition of copper nitrate at 450 °C for 4 h.

2.2. Synthesis of hydrotalcite-like $M_xAl_y(OH)_6NO_3\cdot xH_2O$ ($x = Cu + Zn$)

The procedure for preparation of Cu/Zn/Al-hydrotalcite-like precursor has been described in previous reports [17–19]. Under the condition of vigorous stirring, a solution containing NaOH (∼1.80 M) and Na_2CO_3 (∼0.3 M) was gradually dropped into a solution containing $Cu(NO_3)_2\cdot 2.5\,H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, and $Al(NO_3)_3\cdot 9H_2O$ salts. The pH value was maintained at a value of 9.0 ± 0.3 during the whole dropping operation. The resulting product was aged at 65 °C for 12 h then filtered, washed thoroughly, and dried. The obtained product is then calcined at 450 °C for 4 h. The sample is denoted as LDH.

2.3. Impregnation of copper nitrate onto ZnO-Al_2O_3

A ∼2.0 M NaOH solution is gradually dropped into metal salt solution containing $Zn(NO_3)_2\cdot 6H_2O$, and $Al(NO_3)_3\cdot 9H_2O$ with strong stirring until the precipitation is complete. The resulting product is then filtered, washed completely, and dried. The final product is then calcined at 450 °C for 4 h. A portion of the calcined sample from the above was then used for impregnation of copper nitrate by wet impregnation method using excess amount of water. The solution of copper nitrate (1.57 g in 50 deionized water) was added slowly, with mixing, into the calcined sample (2.0 g). The mixture was then dried overnight at 120 °C and calcined at 450 °C for 4 h. The obtained catalyst is denoted as Cu/ZnO-Al_2O_3.

2.4. Cu/Zn/Al supported on MCM-41

Mesoporous molecular sieve of MCM-41 type in silicalite form was prepared according to the procedure described in our previous report [20]. The supported catalyst was prepared by wet impregnation method. A 15 ml solution containing copper nitrate, zinc nitrate and aluminum nitrate was added slowly into MCM-41 powder with mixing, the mixture was then dried overnight at 95 °C and calcined at 450 °C for 4 h. The prepared catalyst is listed as CZA/MCM-41.

2.5. Co-precipitation of metal nitrates

It should be noted that all the Cu/Zn/Al catalyst samples were prepared using the fixed feed composition of Cu nitrate/Zn nitrate/Al nitrate = 32.87:42.56:24.57 (wt.%), for preparation involving metal nitrates of copper, aluminum and zinc. An ethanol solution of 250 ml containing metal nitrates of copper, aluminum and zinc and a precipitating solution of 63 ml containing oxalic acid in ethanol were simultaneously dropped into deionized water at pH value of 6.5–7.0. The volume of precipitates prepared by this method is shrunk to around 1/4–1/5 of its original volume after drying, which is not observed in the co-precipitation of those salts with sodium carbonate and sodium hydroxide. The sample prepared by this co-precipitation method is denoted as CZA.

2.6. Characterization of the samples

The bulk phase of the synthesized hydrotaclite-like LDH material and its calcined product were examined by X-ray diffraction. Chemical analysis of the sample composition (Cu, Zn and Al) was carried out by using ICP–ES. BET surface areas of the prepared samples were measured by conventional liquid nitrogen adsorption. The reduction properties of the obtained samples were measured by temperature-programmed reduction (TPR) method. About 0.150 g of the calcined sample was placed in a quartz reactor, argon was first used to sweep through the sample until the baseline recorded by TCD is stable, then the sample was reduced up to 800 °C in a gas mixture consisting of 5% H_2–Ar at a heating rate of 10 °C/min. The reduction signal is detected by TCD.

2.7. Catalytic test and product analysis

Methanol steam reforming was carried out in a fixed-bed down-flow reactor under the following conditions: reaction temperature: 230 °C; carrier gas of He: 80 ml/min; catalyst loading: 0.30 g; liquid feed (H_2O/methanol = 1.43 molar ratio): 2 ml/h; WHSV = $5.8\,h^{-1}$. For oxidative steam reforming, oxygen was used with the O_2/methanol molar ratio varying from 0.158 to 1.264. Prior to reaction, the catalyst was reduced at 350–450 °C for 2 h in the flow of pure hydrogen at a rate of 15 ml/min, and then cooled down to the reaction temperature. The gas products were analyzed by GC–TCD with two columns of 6′ SIL Gel/3′MOL Sieve. Liquid products were analyzed by GC with FID.

For comparative evaluation of our laboratory catalysts for methanol reforming, we also conducted tests using a commercial catalyst, Katalco 83-3, obtained from Synetix, which is a low temperature water-gas-shift catalyst. Its typical chemical composition is as follows: CuO, 51 wt.%; ZnO, 31 wt.%; and Al_2O_3, balance.

3. Results and discussion

3.1. Catalyst preparation and characterization

Hydrotalcite-like layered double hydroxides (LDHs) or anionic clays are an important class of materials which have typical composition of $M_{1-x}{}^{2+}M_x{}^{3+}(OH)A_{x/n}{}^{n-}yH_2O$, where M^{2+} and M^{3+} represent metal ions occupying octahedral positions in the hydroxide layers, and A is gallery anion. Because of the changeable ions among M^{2+}, M^{3+} and A^{n-}, the acid–base properties of LDHs can be tailored according to the needs. Here, M^{2+} is replaced by the ions of Cu^{2+} and Zn^{2+}, and M^{3+} by Al^{3+} ion. The composition is similar to typical methanol synthesis catalyst. This could be interesting for employing this kind of material into hydrogen production in methanol reaction, as proven by Suzuki and co-workers [13,14].

Fig. 1 shows the XRD patterns of the typical sample of layered double hydroxides (LDHs) synthesized in this work. The major phase of hydrotaclite-like layered double hydroixde (LDH) can be observed in the sample. The presence of (0 0 3) and (0 0 6) reflections reveals the layer ordering in the *C*-axis direction, and the reflections of (0 1 2) and (0 1 5) can be assigned to the hydrotalcite property, which is in good agreement with the literature [17–19]. Under the same synthesis conditions, the crystal phase purity of LDH, however, greatly depends on the ratio of (Zn + Cu)/Al. The high-purity phase of LDH can be obtained at lower molar ratio of M^{2+}/M^{3+}. In the present work, the synthesis molar ratio of (Zn + Cu)/Al is 1.98. When this ratio is higher than 2.50, besides LDH phase, other phases such as bayerite, $Al(OH)_3$, and aurichalcite will be also present in the samples, as also demonstrated by other researchers [21].

After the sample was calcined at 450 °C, the XRD patterns have been changed dramatically, as can be seen from Fig. 2. In fact, the structure has been mostly destroyed due to thermal decomposition causing the removal of hydroxyl groups from the brucite layers as water and the loss of interlayer carbonate anions as carbon dioxide [22], and the phase composition is typical oxide phase, ZnO + CuO, which is in a good agreement with the results of TGA–DTA [18].

The reduction properties of the copper oxides from the different samples were examined by temperature-programmed reduction (TPR) with hydrogen, and the typical reduction results are shown in Fig. 3. From the spectra it can be seen that CuO from decomposition of copper nitrate displays, not surprisingly, the highest reduction peak temperature at above 450 °C. CuO on ZnO–Al_2O_3 is much easier

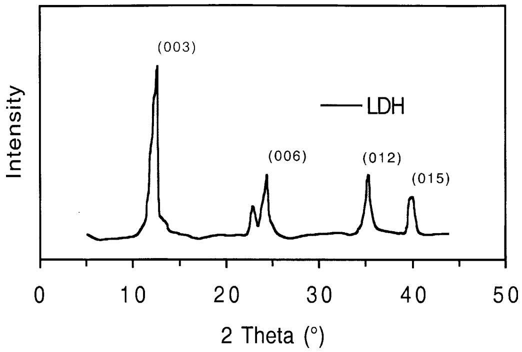

Fig. 1. XRD pattern of the synthesized hydrotalcite-like layered double hydroxide (LDH) before calcination.

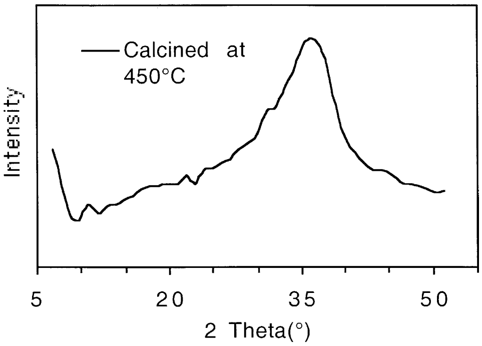

Fig. 2. XRD pattern of the calcined hydrotalcite-like layered double hydroxide (LDH).

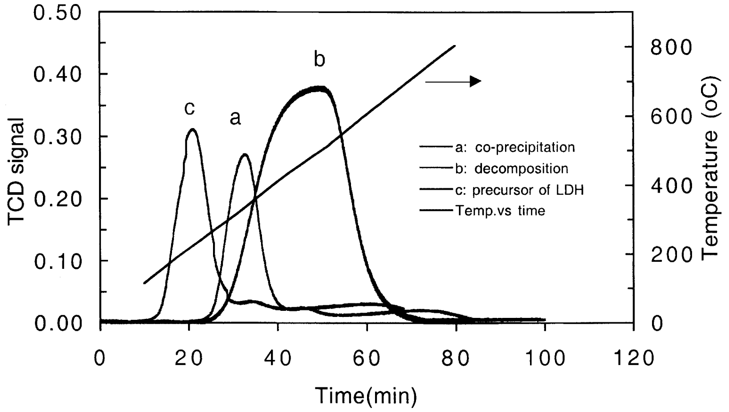

Fig. 3. TPR spectra of the copper-based samples prepared by different methods. (a) From impregnation of copper nitrate onto co-precipitated ZnO-Al_2O_3; (b) from decomposition of copper nitrate; (c) from precursor of LDH.

to reduce, with a peak TPR temperature much lower than the bulk phase CuO from direct decomposition. It is interesting to note that the reduction temperature of copper in the sample CZA/MCM-41, prepared by impregnation of metal nitrates onto MCM-41 shows similar TPR peak temperature with that of CuO sample, but higher than that of Cu/ZnO-Al_2O_3 although both have similar copper content.

More interestingly, the copper oxides from the precursor LDH shows much lower reduction temperature, ~230 °C, compared to the other samples. Table 1 summarizes CuO reduction temperature from the different samples. It can be seen that the CuO reduction temperature can be listed in the order of LDH (230 °C) ~ CZA (233 °C) $<$ Cu/ZnO-Al_2O_3 (327 °C) $<$ CuO (475 °C) ~ CZA/MCM-41 (477 °C). Thus, metal reduction properties can be selectively tailored by the different preparation method.

From the chemical composition listed in Table 1, it can be found that for the impregnated samples, CuO/ZnO-Al_2O_3 and CZA/MCM-41, the content of copper does not change so much as compared with the feed composition during the preparation (32.87 mol%). However, the composition of synthesized samples, LDH and CZA, are quite different from the feed composition (Cu/Zn/Al = 32.87/42.56/24.57 mol). It is interesting to note that the surface area of the samples is in the range of 60–94 m^2/g. The surface area data shown in Table 1 suggests that Cu/ZnO-Al_2O_3 prepared through impregnation has lower surface area (77.3 m^2/g) than that from LDH precursor (84.5 m^2/g). The catalyst CZA from our unique co-precipitation method has the highest surface area (93.7 m^2/g) among all the catalysts prepared. It is interesting to note that low surface area for catalyst CZA/MCM-41, although the surface area of MCM-41 is usually much higher, up to 1000 m^2/g. Perhaps the solution of metal nitrate showing strong acid character (pH value $<$ 2.0) destroys MCM-41 structure (which has weak

Table 1
The reduction properties, chemical composition and BET surface area of the samples

Sample	CuO	Cu/ZnO-Al_2O_3	CZA/MCM-41	LDH	CZA
Reduction peak (°C)	475	327	477	230	233
Composition (mol%)					
Cu	100	30.7	31.58	42.31	45
Zn	0	45.3	42.52	40.56	42.75
Al	0	23.91	25.86	17.17	12.25
BET (m^2/g)	~	77.3	63.9	84.5	93.7

resistance to acid) during the preparation and heat treatment.

3.2. Steam reforming of methanol

Methanol conversion over the above catalysts was investigated under the condition of steam reforming. The main products are hydrogen and carbon dioxide as well as a minor product, carbon monoxide; no other product was detected. The catalyst activity data are shown in Fig. 4. From catalyst activity in methanol conversion shown in Fig. 4 it can be found that overall catalysts appear to be relatively stable during the period of 3 h test. The supported catalyst, CZA/MCM-41, shows the lowest activity, only around 15%, during methanol steam reforming, however, the catalyst Cu/ZnO-Al_2O_3 prepared by impregnation of copper nitrates exhibits the enhanced activity to methanol conversion, which is around 70–75%. The catalyst from the precursor of LDH shows even higher activity as compared with Cu/ZnO-Al_2O_3. Interestingly, methanol is totally converted over catalyst CZA by co-precipitation. By correlation of surface area in Table 1, it is clear that the preparation method plays a key role in methanol conversion. In correlation with their reduction properties (Table 1), it can be seen that those with lower CuO reduction temperature (that also corresponds to high surface area) shows high activity to methanol conversion during steam reforming. These trends are consistent with the very recent results reported by Segal et al. [23] and are also in line with the reports on LDH materials [13].

The easier reduction of CuO in the sample might result from its fine dispersion and larger surface according to the suggestion by Suzuki and co-workers [13,14]. Thus, Cu/Zn/Al catalyst with high surface area could have an advantage for the dispersion of copper particle. Reforming of methanol with a more active catalyst would favor methanol conversion more at lower temperature, and, therefore, can decrease CO content in the hydrogen-rich gas from methanol conversion by suppressing methanol decomposition (reaction in Eq. (a)) and minimizing the reverse water-gas-shift reaction (Eq. (g)). Unfortunately, Cu/Zn/Al catalysts prepared from conventional methods such as sequential precipitation, co-precipitation by using sodium carbonate and sodium hydroxide and from the precursor like LDH (surface area is higher than precipitation) appear to have relatively low surface area (in the range of 70–100 m^2/g). Thus, the search for Cu/Zn/Al with higher surface area and high dispersion of copper particle could be more interesting in the study of methanol conversion.

It can be seen from the yields of H_2 and CO_2 shown in Figs. 5 and 6, respectively, that H_2 yield has the same trends as methanol conversion. Over catalysts LDH and CZA, H_2 yield is around 70–75%, and CO_2 yield (Fig. 6) over both catalyst is around 20–25%. The molar ratio of H_2/CO_2 is roughly around 3:1, indicating that the methanol conversion over LDH and

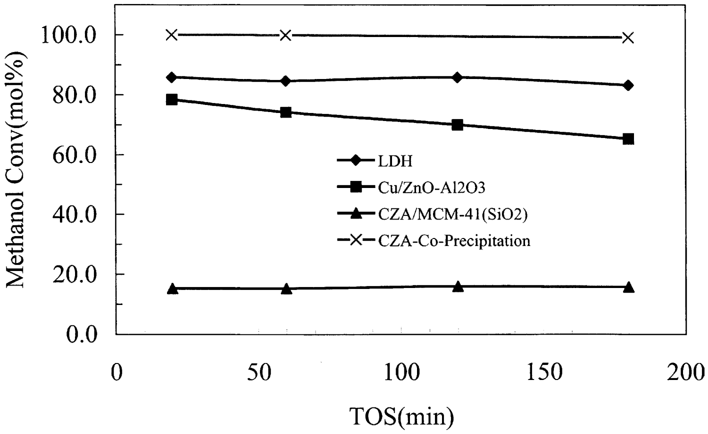

Fig. 4. Methanol steam reforming over the different catalysts as a function of time. Reaction temperature: 230 °C; WHSV = 5.8 h^{-1}; liquid feed (water/methanol = 1.43 mol ratio): 2 ml/h; carrier gas He: 80 ml/min; catalyst: 0.30 g.

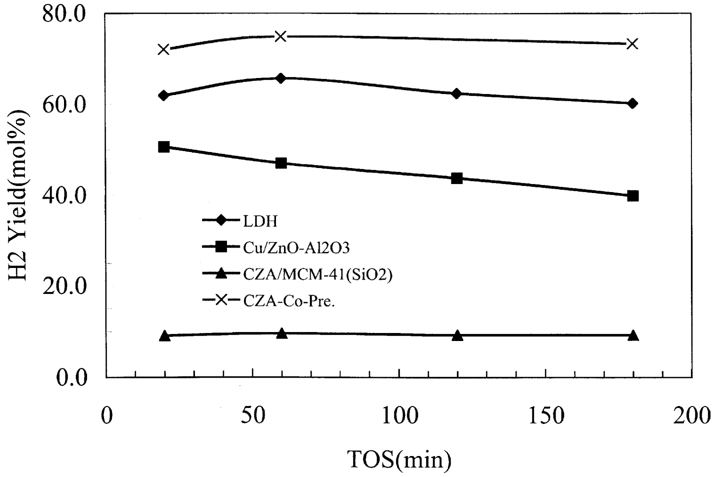

Fig. 5. Yield of hydrogen in the products during steam reforming of methanol over catalysts. Reaction temperature: 230 °C; WHSV = 5.8 h^{-1}; liquid feed (water/methanol = 1.43 mol ratio): 2 ml/h; carrier gas He: 80 ml/min; catalyst: 0.30 g.

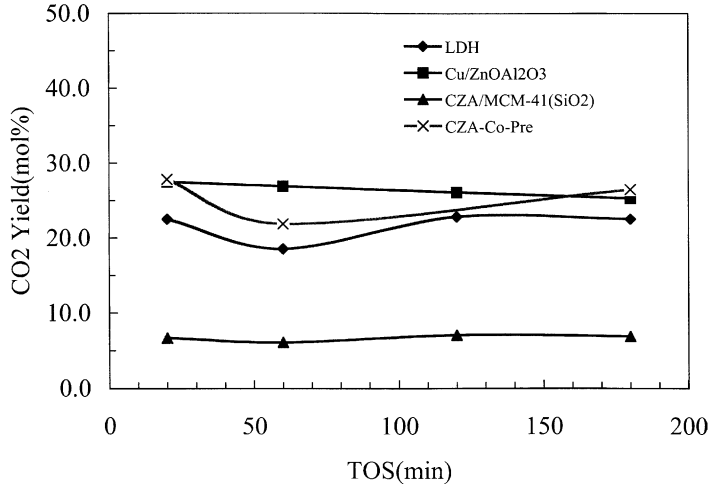

Fig. 6. Yield of CO_2 in the products during steam reforming of methanol over catalysts. Reaction temperature: 230 °C; WHSV = 5.8 h^{-1}; liquid feed (water/methanol = 1.43 mol ratio): 2 ml/h; carrier gas He: 80 ml/min; catalyst: 0.30 g.

CZA proceeds according to the Eq. (c), the typical steam reforming.

Upon achieving high conversion of methanol, the most important concern is CO content in the product. As shown in Fig. 7, CO yield is around 0.5% over LDH catalyst. CZA produces much lower CO in the products, and its activity is 15% higher than LDH. These results imply that this CZA catalyst can effectively depress the formation of CO during methanol steam reforming; the reason for that is under investigation. It is interesting to note that CO formation over catalyst CZA/MCM-41 is below our GC detection limit (250 ppm).

A brief comparison of CZA was made with a commercial catalyst from Synetix, catalyst Katalco 83-3 (low temperature water-gas-shift catalyst from Synetix, with the following chemical composition: CuO 51 wt.%, ZnO 31 wt.% and Al_2O_3 balance). The

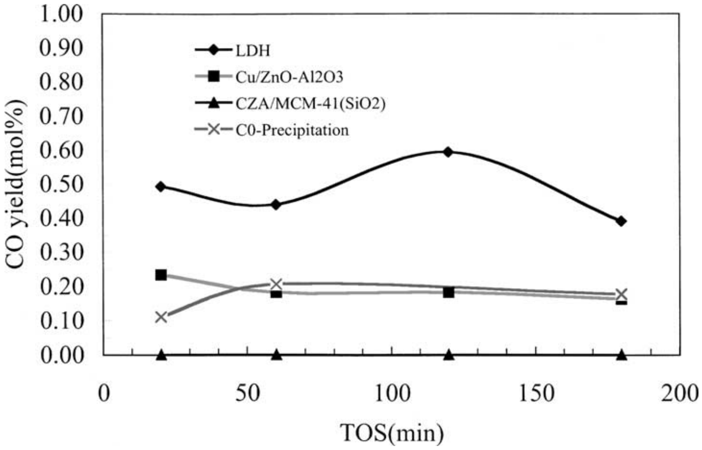

Fig. 7. Yield of CO in the products during steam reforming of methanol over catalysts. Reaction temperature: 230 °C; WHSV = 5.8 h^{-1}; liquid feed (water/methanol = 1.43 mol ratio): 2 ml/h; carrier gas He: 80 ml/min; catalyst: 0.30 g.

results are shown in Figs. 8 and 9. Under the test conditions both catalyst show high ability to convert methanol (~100%, Fig. 8) and the yields of hydrogen and carbon dioxide also show similar patterns with ~75% of H_2 and ~25% of CO_2. However, CO formation over the two catalysts are significantly different, CZA produces only around 0.2% CO, near three times less than that with the commercial catalyst (~0.55%). More work on CZA physicochemical properties is under way.

3.3. *Oxidative steam reforming of methanol*

To further investigate the catalyst performance of CZA for oxidative steam reforming of methanol, oxygen was added under the same reaction conditions and the results are shown in Table 2. Two different O_2/MeOH ratios were tested at constant H_2O/MeOH ratio of 1.43. Similar to steam reforming, over both catalysts methanol is almost completely converted into hydrogen, CO_2 and CO. At an O_2/methanol ratio

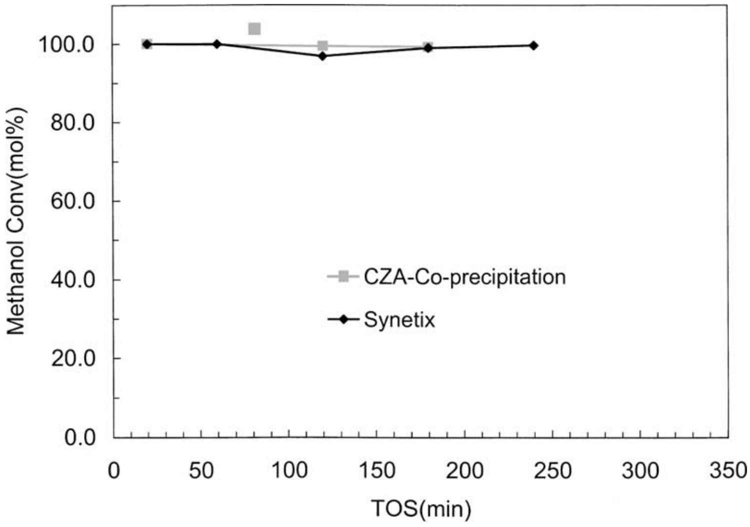

Fig. 8. Comparison of catalyst activity between CZA and the commercial catalyst during methanol steam reforming.

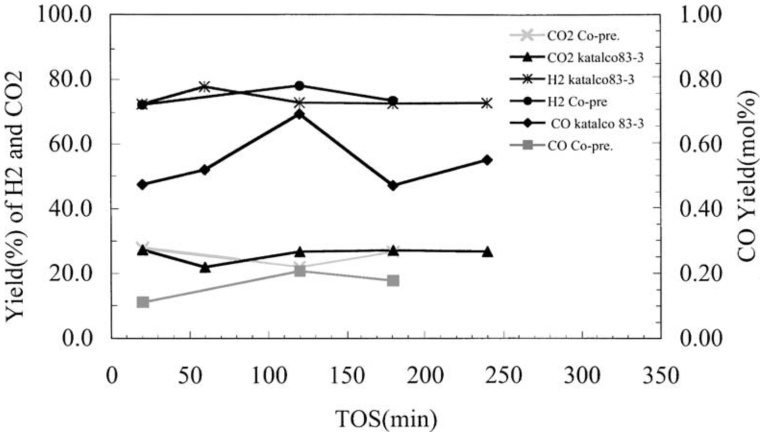

Fig. 9. Comparison of the product distribution between CZA and the commercial catalyst during methanol steam reforming.

of 0.158, CZA and the commercial Katalco 83-3 catalyst gave similar methanol conversions (99.5 versus 98.7%) and H_2 yields (75.9–76.0%). However, the CO concentration with CZA was 0.15%, much lower than that (0.54%) with Katalco 83-3. In terms of the effects due to O_2 on the product distribution over CZA, the addition of oxygen at lower ratio of O_2/methanol (0.158) appears to increase the concentration of hydrogen and CO, and decrease the formation of CO_2. This could imply the occurrence of partial oxidation of methanol into hydrogen and CO. When the O_2/methanol ratio was increased from 0.158 to 0.474, the H_2 yield with CZA decreased and the CO concentration also decreased to as low as 0.05%. The removal of CO appears to take place over CZA with increasing oxygen, since CO decreased from 0.11 to 0.05%. This CO reduction corresponds to the consumption of hydrogen and formation of more CO_2 with increasing O_2/methanol ratio with CZA. The decrease of hydrogen and CO may be attributed to the reactions of hydrogen and CO with oxygen into CO_2 and H_2O, respectively. On the other hand, this level of increase did not affect H_2 yield but increased CO concentration (from 0.535 to 0.853%) with Katalco 83-3. The decrease in CO concentration with Katalco 83-3 was observed only when O_2/methanol ratio was increased to as high as 1.264, which reduced CO from 0.853 to 0.031% and also decreased H_2 yield from 76.55 to 68.41%, as shown in Table 2.

From the above it seems that oxygen prefers to react with hydrogen. The highly preferential reaction of CO with oxygen (that is known to occur over precious metal, such as Pt), is not observed over the Cu/Zn/Al catalysts, although the selectivity for CO oxidation seems to be better with the laboratory-prepared CZA than with the commercial catalyst. In other words, the

Table 2
Comparison of the effect of O_2 on methanol steam reforming over the catalysts CZA and Katalco 83-3

	0		0.158		0.474		1.264
	CZA	Katalco 83-3	CZA	Katalco 83-3	CZA	Katalco 83-3	Katalco 83-3
O_2/methanol (mol)							
TOS (min)	20	20	30	30	30	30	30
Conversion (mol%)	99.56	99.87	99.54	98.67	100	100	100
H_2, yield (mol%)	72.078	71.992	75.977	75.977	71.050	76.555	68.407
CO, yield (mol%)	0.111	0.426	0.154	0.535	0.054	0.853	0.031
CO_2, yield (mol%)	27.812	27.582	26.116	23.488	28.944	22.592	31.562

Reaction conditions: temperature: 230 °C; carrier gas He: 80 ml/min; catalyst: 0.300 g; feed (H_2O:methanol = 1.43 mol) 2 ml/h; TOS: 60 min.

much lower CO concentration in the product with CZA is due largely to the ability of the catalyst prepared in our laboratory towards suppressing CO formation, and the oxidation of CO, once formed, is a secondary reaction that accounts for some further reduction in CO concentration.

4. Conclusions

Several methods including impregnation, co-precipitation and hydrothermal synthesis were employed for the preparation of catalyst for methanol steam reforming, and the catalytic results show that the preparation method plays an important role in the methanol steam reforming.

The catalyst with lower copper-reduction temperature shows higher activity to produce hydrogen from methanol steam reforming. The catalyst CZA prepared by a proper co-precipitation method in our laboratory shows high performance with high methanol conversion and low CO formation in the products at a lower reaction temperature, when compared to the commercial catalyst and laboratory catalysts prepared by other methods.

Oxidative steam reforming was examined at 230 °C over the same catalysts. The CO concentration with the catalyst CZA was as low as 0.05% when O_2/MeO ratio and H_2O/MeOH ratio were 0.47 and 1.43, respectively. The highly selective or preferential oxidation of oxygen with CO was not observed during the oxidative steam reforming of methanol over Cu/Zn/Al catalyst.

Acknowledgements

The flow reactor system was set up with kind help from Dr. Srinivas T. Srimat and the sample of MCM-41 was kindly supplied by Dr. Xiaochun Xu in our laboratory at Penn State University.

References

[1] C. Song, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (1) (2001) 8.

[2] S. Imamura, T. Higashihara, Y. Saito, H. Aritani, H. Kanai, Y. Matsumura, N. Tsuda, Catal. Today 50 (1999) 369.

[3] Y. Matsumura, K. Kuraoka, T. Yazawa, M. Haruta, Catal. Today 45 (1998) 191.

[4] M.L. Cubeiro, J.L.G. Fierro, Appl. Catal A: Gen. 168 (1998) 307.

[5] J.L.G. Fierro, Stud. Surf. Sci. Catal. 130 (2000) 177–186.

[6] E. Newson, P. Mizsey, T. Truong, P. Hottinger, Stud. Surf. Sci. Catal. 130 (2000) 695.

[7] T.L. Reitz, S. Ahmed, M. Krumpelt, R. Kumar, H.H.. Kung, Stud. Surf. Sci. Catal. 130 (2000) 3645.

[8] N. Ellis, S.R. Edwards, J.C. Frost, S.E. Golunski, A.N.J. van Keulen, N.G. Lindewald, J.G. Reinkingh, J. Power Sources 71 (1-2) (1998) 123.

[9] L. Ma, G. Gong, T. Tran, M.S. Wainwright, Catal. Today 63 (2000) 499.

[10] J.P. Breen, J.R.H. Ross, Catal. Today 51 (1999) 521.

[11] S.P. Asprey, B.W. Wojciechowski, B.A. Peppley, Appl. Catal. A: Gen. 179 (1-2) (1999) 70.

[12] B.A. Peppley, J.C. Amphlett, L.M. Kearns, Appl. Catal. A: Gen. 179 (1-2) (1999) 21.

[13] S. Velu, K. Suzuki, T. Osaki, Chem. Commun. (1999) 2341

[14] S. Velu, K. Suzuki, M. Okazaki, M.P. Kapoor, T. Osaki, F.J. Ohashi, Catalysis 194 (2) (2000) 373.

[15] K. Geissler, E. Newson, F. Vogel, T.B. Truong, P. Hottinger, A. Wokaun, Phys. Chem. Chem. Phys. 3 (3) (2000) 289.

[16] G.E. Parries, K. Klier, J. Catal. 97 (1986) 374.

[17] J. Guo, Q.Z. Jiao, J.P. Shen, Z. Jiang, G.H. Yang, Z. Min, Catal. Lett. 40 (1/2) (1996) 43.

[18] J. Guo, Q.Z. Jiao, J.P. Shen, H.J. Lu, D. Liu, Z. Jiang, Z. Min, Acta Chim. Sinica 54 (4) (1996) 357.

[19] J. Guo, T. Sun, J.P. Shen, D. Liu, Z. Jiang, Z. Min, Chem. J. Chin. Universities 16 (4) (1995) 512.

[20] K.M. Reddy, C. Song, Catal. Lett. 36 (1996) 103.

[21] Y. Lwin, M. Yarm, Z. Yaakob, A. Mohamad, W.R. Wan, Daud. Mater. Res. Bull. 36 (2001) 193.

[22] V. Rives, S. Kannan, J. Mater. Chem. 10 (2000) 489.

[23] S.R. Segal, K.B. Anderson, K.A. Carrado, C.L. Marshall, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (2) (2001) 654.