Short communication

Activity and stability enhancement of copper–alumina catalysts using cerium and zinc promoters for the selective production of hydrogen via steam reforming of methanol

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Abstract

The catalytic activity and hydrogen selectivity of cerium and zinc promoted copper–alumina catalysts have been investigated for the selective production of hydrogen via steam reforming of methanol (SRM). The SRM was carried out in a fixed bed tubular reactor at atmospheric pressure over a temperature range 200–300 °C. The major reaction products were hydrogen and carbon dioxide with traces of carbon monoxide. Catalysts of varying compositions were prepared by the wet impregnation method and characterized by atomic absorption spectroscopy (AAS), BET surface area, pore volume, pore size, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and thermogravimetry analysis (TGA). Results revealed that the methanol conversion, hydrogen selectivity and carbon monoxide formation varied with the type of promoter and content of copper in the catalyst. Cerium promoted Cu–Zn–Ce–Al-oxide catalysts improved the activity and hydrogen selectivity greatly and also kept the CO formation very low. Using cerium the SRM could be carried out at lower temperature with high methanol conversion, results in suppression of methanol decomposition and reverse water gas shift reactions eventually end-up with the low carbon monoxide and hydrogen rich product stream. Cerium also stabilizes the copper–alumina catalysts effectively that was confirmed by deactivation studies in which cerium promoted Cu–Zn–Ce–Al-oxide catalysts gave the consistent performance for a long run-time compared to catalysts containing only zinc promoter. The optimum operating conditions for SRM have been investigated by detailed study of effects of reaction temperature, contact time and steam to methanol molar ratio on methanol conversion, hydrogen selectivity and CO formation. Reaction pathway has been proposed for the SRM based on results obtained.
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*Keywords:* SRM; Hydrogen; Cu–Zn–Ce–Al-oxide catalysts

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are being actively considered for the automotive applications to lower the fuel consumption and to reduce the harmful emissions [1]. The pure hydrogen is a superior PEM fuel cell feed but distribution and storage difficulties pose serious disadvantages to its direct use for the fuel cell propulsion systems [2]. Therefore on-board hydrogen production from a suitable liquid hydrocarbon sources appears to be a practical option. Methanol is preferable to other liquid hydrocarbon sources because it has high hydrogen to carbon ratio, can be reformed at relatively low temperature, free of sulfur compounds [3]. For the conversion of methanol to hydro-gen different chemical reactions can be applied. The simplest option is the methanol decomposition (MD):

$$CH_3OH \leftrightarrow CO + 2H_2, \quad \Delta H^\circ = 91 \, kJ \, mol^{-1} \quad (1)$$

Yielding hydrogen and carbon monoxide. However, the high content of latter in the product gas makes this reaction unsuitable for the PEM fuel cell applications. Another reaction is partial oxidation of methanol (POM):

$$CH_3OH + 1/2O_2 \leftrightarrow CO_2 + 2H_2, \quad \Delta H^\circ = -192.3 \, kJ \, mol^{-1} \quad (2)$$
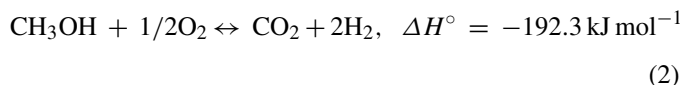
Reaction (2) is a highly exothermic which leads the problem of heat removal, reactor temperature control and also produces significant amount of CO. The promising route is the steam

reforming of methanol (SRM):

$$CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2, \quad \Delta H^\circ = 49 \, kJ \, mol^{-1}$$

(3)
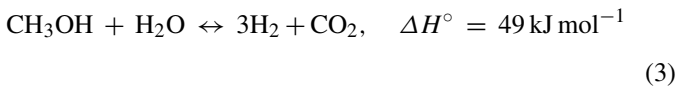
Of all the considered reactions, it offers highest maximum hydrogen product gas (75%). Several authors have discussed the preparation, characterization and activity of Cu–Zn–Al-oxide catalysts for a steam reforming of methanol [4–6], but very less work has been done towards the study of deactivation of catalysts and stabilization of them [6–7]. Therefore in the present study an attempt has been made to develop the stable catalyst by incorporating ceria in Cu–Zn–Al-oxide catalysts. The long-term activity of catalyst is essential for the automobiles operated by PEM fuel cell to avoid the frequent replacement of reformer catalysts. Ceria also affects the degree of dispersion as well as redox behavior and catalytic activity of supported catalysts [8]. Cu/Ce based oxide catalysts have been used extensively for the water gas shift reaction [9]. The CO formation using Cu–Zn–Al-oxide catalysts is also quite high compared to allowable 20 ppm CO in the hydrogen rich feed stream of PEM fuel cell to avoid the damage of Pt anode of PEM fuel cell. In this work CO formation has been reduced significantly compared to Cu–Zn–Al-oxide catalysts by developing Cu–Zn–Ce–Al-oxide catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

All the catalysts used in the present study were prepared by a wet impregnation method using copper, zinc and cerium nitrates. Alumina pellets were dipped in the excess nitrate solution for 4 h under vigorous stirring followed by removal of excess water in a rotary vacuum evaporator. Impregnated pellets were dried for 12 h at 125 °C followed by calcination, to convert nitrates in to oxides, in the presence of air at 350 °C for 4 h. The same procedure was followed to prepare Cu–Zn–Al-oxide catalysts. Surface area, pore volume and pore size of the catalysts were measured by BET method using N_2 adsorption isotherm recorded at −196 °C in a Micromeritcs ASAP 2010 equipment. The final composition of the catalysts was determined by atomic absorption spectroscopy (AAS) Varian AA420FS. Different crystalline

phases of catalysts were identified by X-ray powder diffraction (XRD) using Philips X'PERT PW1827/21 powder diffractometer. Morphology and structure of the catalysts were studied using Cambridge 360 scanning electron microscope (SEM). Surface analysis of post reaction catalysts was done by X-ray photoelectron spectroscopy (XPS) using Perkin-Elmer-1257 at a base pressure 5×10^{-8} Torr with dual anode Al Kα 1253.6 eV X-ray source. The amount of carbon deposited on the catalysts was determined using Seiko TG/DTA 32 SSC 5100 thermogravimetric analyzer (TGA).

2.2. Catalytic activity

Catalytic activity test experiments were carried out in a continuous flow fixed-bed reactor (19 mm i.d.) placed in an electrically heated furnace equipped with PID temperature controllers and thermocouples. The experiments were conducted over a reaction temperature range of 200–300 °C at atmospheric pressure with 3 g of the catalyst loading in the reactor. The catalysts were reduced in situ before SRM reaction in a stream of H_2/N_2 (5:95 v/v) gas flow for which heating was done from room a temperature to 240 °C at the rate of 1 °C min^{-1}, and kept at 240 °C for 3 h. The SRM was carried out in the reactor by feeding the preheated methanol and water vapor mixture along with nitrogen as an inert carrier at a designated temperature and contact time. Products were analyzed using Nucon-5700 Gas chromatograph.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the chemical composition, surface area, pore volume and average pore size of the different catalysts. The BET surface area and pore volume of Cu–Zn–Al-oxide catalysts decreased with increasing copper loading, and for Cu–Zn–Ce–Al-oxide catalysts appropriate amount of incorporation of ceria gave the highest surface area, i.e. 162 m^2 g^{-1} for 3CZCeA (Cu/Zn/Ce/Al:10/5/3/82) catalyst. The final elemental compositions of all the catalysts were found less compared to that were taken stoichiometrically due to attrition and heat treatment during catalyst preparation. XRD patterns as shown

Table 1
Physiochemical properties of catalysts

	Cu/Al	Cu/Zn/Al		Cu/Zn/Ce/Al				
	CA	1CZA	2CZA	1CZCeA	2CZCeA	3CZCeA	4CZCeA	5CZCeA
Comp[a] (mol%)	15/85	15/5/80	10/5/85	15/5/5/75	12/5/5/78	10/5/3/82	10/5/2/83	8/4/2/86
Comp[b] (mol%)	14/86	14/4/82	9.5/5/85.5	14/4.5/4.5/77	11.5/5/5/78.5	9.5/4.5/3/83	9.5/5/2/83.5	7.6/3.5/2/86.9
S_{BET} (m^2 g^{-1})	112	133	152	122	129	162	156	151
V_{pore} (cm^3 g^{-1})	0.26	0.29	0.34	0.23	0.27	0.36	0.33	0.33
D_{avg} (Å)	47	56	61	54	57	61	58	59
$X_{methanol}$[c] (%)	31	64	76	57	54	90	84	70
H$_2$ rate[c] (mmol s^{-1} kg$_{cat}$$^{-1}$)	81	171	203	152	146	244	228	188
CO[c] (mol%)	3	1.4	1.1	1.1	0.09	0.06	0.07	1

[a] Stoichiometric composition.
[b] Final composition.
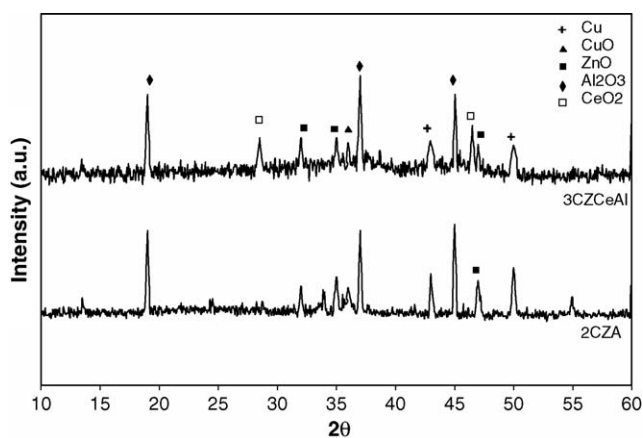[c] $W/F = 11 \, kg_{cat} \, mol^{-1} \, s$, $T = 260$ °C, $S/M = 1.4$ M.

Fig. 1. X-ray diffraction patterns of reduced catalysts before SRM.

in Fig. 1 revealed that on the reduction CuO reduced to Cu for all the catalysts, while Zn, Ce and Al remained in oxide form. SEM images suggested that there was no morphological change in the catalysts after SRM reaction.

3.2. Evaluation of catalytic performance

Table 1 compares the activity of alumina supported copper catalysts modified with zinc oxide and ceria at a temperature of 260 °C. The Cu–Al$_2$O$_3$ catalyst exhibited only 31% methanol conversion, which comply to use the promoters. Among Cu–Zn–Al-oxide catalysts maximum methanol conversion 76% and hydrogen rate 203 mmol s^{-1} kg$_{cat}$$^{-1}$ was obtained with the 2CZA (Cu/Zn/Al:10/5/85) catalyst at 260 °C. For these catalysts the excessive loading of copper did not perform well which might be due to formation of larger copper crystallites that resulted in low surface area. Catalysts modified by CeO$_2$ along with ZnO showed significant enhancement not only in terms of methanol conversion but also in terms of H$_2$ production rate and minimization of CO formation. The excessive loading of Cu and Ce was leading to the lower activity as in the case of 1CZCeA (Cu/Zn/Ce/Al:15/5/5/75) and 2CZCeA (Cu/Zn/Ce/Al:12/5/5/78); moreover for the optimum 10 mol% Cu loading, if Ce mol% decreased the activity also got deteriorated as in the case of 4CZCeA (Cu/Zn/Ce/Al:10/5/2/83). The above discussion in conjunction with Table 1, suggested that the optimum loading of Cu and Ce was required to enhance the catalyst performance, which was exhibited by 3CZCeA (Cu/Zn/Ce/Al:10/5/3/82). It can be seen that the CO formation was quite low for all the Cu–Zn–Ce–Al-oxide catalysts compared to Cu–Zn–Al-oxide catalysts.

3.3. Role of ceria on catalytic performance

Fig. 2 shows a plot of effect of temperature on the catalytic performance of 3CZCeA at different contact times. The methanol conversion reached 100% at a temperature of 300 °C for the contact time (W/F) 11 kg$_{cat}$ mol^{-1} s. It can also be seen that for a constant temperature the methanol conversion also increased with contact time. Fig. 2 also shows a rise in the
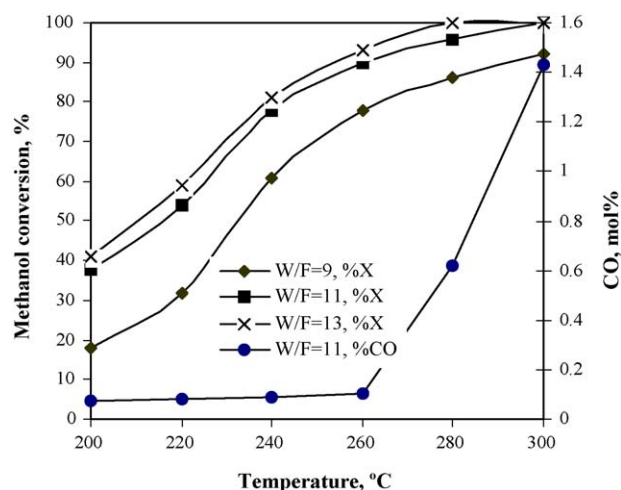

Fig. 2. Effect of reaction temperature on catalytic activity (catalyst: 3CZCeA, S/M = 1.4 M).

CO formation with temperature. The CO formation drastically increased at a temperature more than 260 °C, which might be due to acceleration of reverse water gas shift reaction (rWGS: Eq. (4)):

$$CO_2 + H_2 \leftrightarrow CO + H_2O, \ \Delta H^\circ = 41 \, kJ \, mol^{-1} \qquad (4)$$

It is very much essential to keep the CO concentration as low as possible in hydrogen rich SRM product stream for the PEM fuel cell grade hydrogen production. The CO concentration also went up significantly at higher contact times, typically at more than 11 kg$_{cat}$ mol^{-1} s. Therefore 260 °C and W/F = 11 kg$_{cat}$ mol^{-1} s, can be chosen as the optimum values. Ceria containing Cu–Zn–Ce–Al-oxide catalysts enhanced the activity due to two reasons, firstly use of multi-component precursors which give rise to the well dispersed metal particles on the surface of oxide supports upon calcinations and reduction [10] and secondly the CeO$_2$ has a significant influence on surface copper dispersion of any crystallite sizes [11], which can also be confirmed by the XRD patterns in Fig. 1. It shows that the peak width of Cu phase for 3CZCeA is wider than that for 2CZA, indicating that particle size of Cu in 3CZCeA is smaller, and smaller the crystallites better the copper dispersion.

3.4. Effect of temperature on hydrogen production rate and selectivity

Hydrogen production rate increased with temperature for 3CZCeA as shown in Fig. 3. Contradict, the hydrogen selectivity decreased with temperature. This suggests that at higher temperature the rWGS (Eq. (4)) and MD (Eq. (1)) reactions get accelerated. Based on these we proposed the reaction pathways later. The hydrogen selectivity significantly decreased at the temperature more than 260 °C. Moreover the hydrogen selectivity and production rate were higher at W/F = 11 than those were at W/F = 13 even if methanol conversion was higher for the W/F = 13. Above discussion also suggests the optimum reaction temperature and contact time should be 260 °C and 11 kg$_{cat}$ mol^{-1} s respectively.
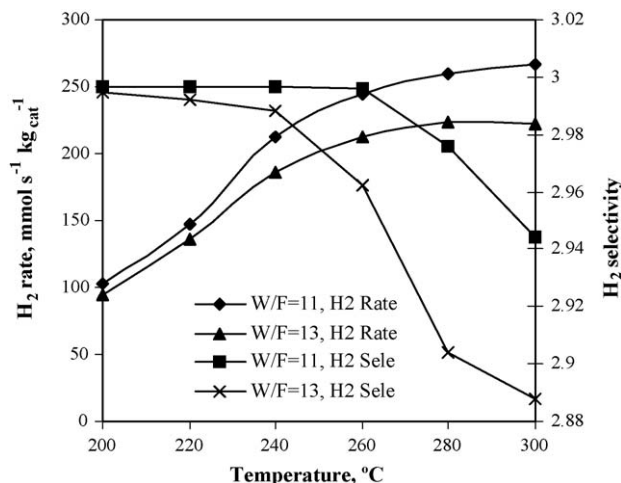
Fig. 3. Hydrogen production rate and selectivity as a function of reaction temperature at different contact times (catalyst: 3CZCeA, $S/M = 1.4$ M).

3.5. Effect of steam to methanol ratio

The steam to methanol molar ratio greatly affected the CO formation as shown in Fig. 4. Remarkably CO formation decreased from 1.9 mol% at $S/M = 1$ to 0.1 mol% at $S/M = 1.4$, and further decreased to 0.09 mol% at $S/M = 1.8$. At the ratio greater than 1.4, there was no significant change in the catalytic activity.

3.6. Durability of catalysts

The Cu–Zn–Al-oxide catalysts face the great problem of deactivation [6–7]. In the present study also methanol conversion decreased by the magnitude of 14% within 20 h run-time for the catalyst 2CZA as shown in Fig. 5. The 3CZCeA exhibited consistent performance, methanol conversion decreased by the magnitude of 3% that is very much essential for a long-term catalyst performance to use it for the on-board PEM fuel cell applications. The reactivation of catalysts in oxidizing atmosphere recovered a part of activity suggesting that coking was the part of cause of activation loss. This was also confirmed
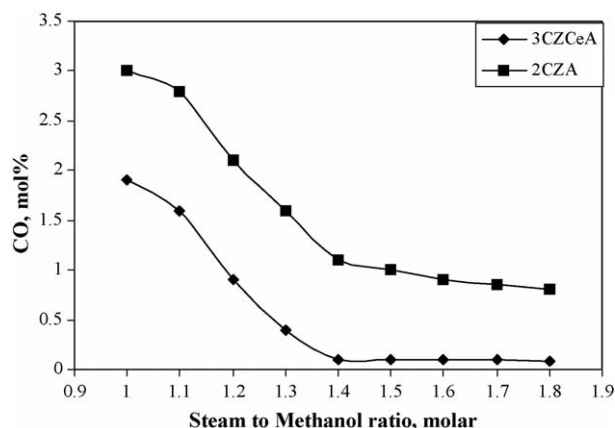

Fig. 4. Effect of steam to methanol ratio on CO formation ($T = 260\,°C$, $W/F = 11\,kg_{cat}\,mol^{-1}\,s$).
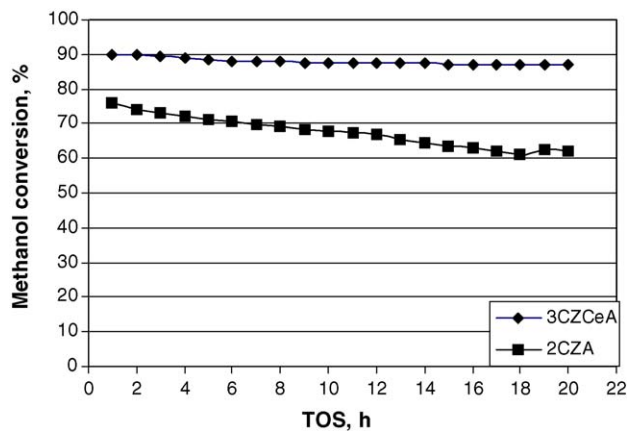

Fig. 5. Time-on-stream stability test of catalysts ($T = 260\,°C$, $W/F = 11\,kg_{cat}\,mol^{-1}\,s$, $S/M = 1.4$ M).

by C 1s XPS spectra as shown in Fig. 6. The different carbon species formed on the surface of catalyst 3CZCeA were, graphite carbon (–C–C– with binding energy 284.9 eV) and oxidized carbon (CO_3 with binding energy 289.5 eV). The amount of coke deposited on the catalysts was 0.14 and 0.06 wt.% for the 2CZA and 3CZCeA respectively at the end of TOS test. Ceria enhanced the stability because it has a high oxygen storage capacity [12], and partially reduced ceria sites formed under the reductive conditions, like SRM process, produce the mobile oxygen that facilitates the coke gasification to inhibit the coke deposition. The ceria also increase the thermal stability to prevent the sintering [13].

3.7. Reaction path way

Based on the results obtained and subsequent discussion, we proposed the following reaction pathway for SRM process. Methanol dehydrogenates to produce methyl formate and hydrogen. Then methyl formate gets hydrolyzed to form formic acid and methanol, followed by decomposition of formic acid to give carbon dioxide:

$$2CH_3OH \leftrightarrow CH_3OCHO + 2H_2 \tag{5}$$

$$CH_3OCHO + H_2O \leftrightarrow CH_3OH + HCOOH \tag{6}$$

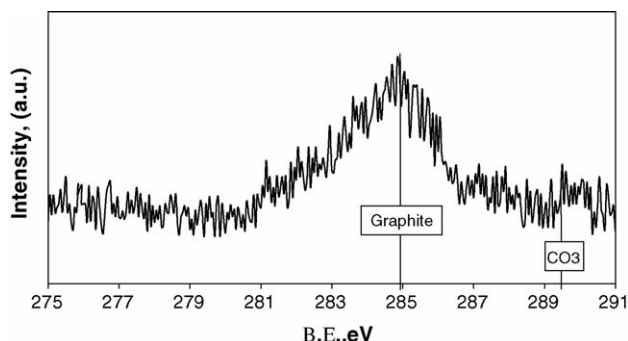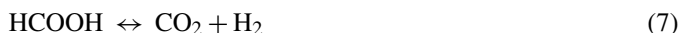$$HCOOH \leftrightarrow CO_2 + H_2 \tag{7}$$

Fig. 6. C 1s XPS spectra of 3CZCeA spent catalyst tested for 20 h TOS.

In the present study methyl formate and formic acid were observed in trace amount at reaction temperature below 200 °C. The above reaction pathway agrees with the reaction mechanism proposed by Jiang et al. [14] who made detailed study of individual reactions (Eqs. (5)–(7)) during kinetic modeling study of steam reforming of methanol over $Cu/ZnO/Al_2O_3$ catalyst. Peppley et al. [15] also confirmed the formation of methyl formate over $Cu/ZnO/Al_2O_3$ catalyst surface for steam reforming of methanol. The selectivity of hydrogen and carbon dioxide decreased with temperature while that of carbon monoxide increased, which suggests that the CO formed as a secondary product from hydrogen and carbon dioxide via reverse water gas shift reaction (Eq. (4)).

4. Conclusions

Cu–Zn–Ce–Al-oxide catalysts exhibited the high activity in terms of methanol conversion, hydrogen selectivity, CO concentration very low up to 600 ppm and long-term stability compared to Cu–Zn–Al-oxide catalysts. Results indicated that the supply of excess steam for the SRM reaction inhibited the CO formation greatly. XRD results revealed that the addition of CeO_2 to Cu–Zn–Al-oxide catalysts could enhance the copper dispersion, which was attributed to the higher catalytic activity. Optimum operating conditions, $W/F = 11\,kg_{cat}\,mol^{-1}\,s$, $T = 260$ °C and $S/M = 1.4\,M$, were suggested to obtain the high methanol conversion and hydrogen production rate, and to keep the CO formation very low to reduce the load on partial oxidation of CO to CO_2 (PROX) before feeding the hydrogen rich stream as a feed for the PEM fuel cells. Incorporation of CeO_2 increased the durability of catalysts by providing thermal stability and coke gasification to minimize the sintering and coking respectively.

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