

Methanol Steam Reforming Catalyzing over Cu/Zn/Fe Mixed Oxide Catalysts

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ABSTRACT

Methanol steam reforming plays a pivotal role in the production of hydrogen for fuel cell systems in a low temperature range. To accomplish higher methanol conversion and lower CO production, the reaction was catalyzed by Cu/Zn/Fe mixed oxides. Various ratios of Fe and Cu/Zn were co-precipitated in differential method to optimize the Cu/Zn/Fe structure. The sample containing 45Cu50Zn5Fe (wt %) revealed its maximum methanol conversion of 98.4 % and CO selectivity of 0.78 % with operating conditions of gas hourly space velocity of 18000 h⁻¹ and steam to carbon molar ratio of 1.3 at 270 °C. The synthesized catalysts were analyzed by powder X-ray diffraction, N₂ adsorption/desorption, temperature programmed reduction, scanning electron microscopy techniques. The results revealed that the prepared samples presented mesoporous structure with different pore size depending on the Cu/Zn/Fe ratios. The results showed that increase in Fe loading to 20 wt % empowered methanol conversion and decreased CO selectivity. Moreover, the optimized catalyst activity was kept constant during 17 h time on stream. Besides, operating conditions of gas hourly space velocity and steam to carbon ratios were evaluated.

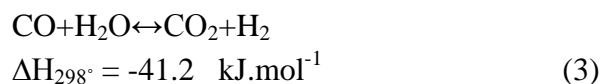
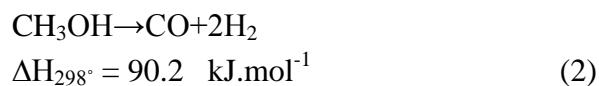
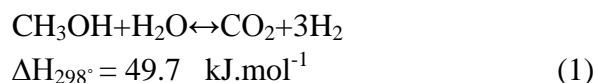
1. Introduction

Fuel cell systems allowing conversion of electrochemical energy to electricity have been addressed to resolve challenges of global pollution [1, 2]. Hydrogen as a main feedstock of polymer exchange membrane fuel cells (PEMFCs), should be pure (CO content < 40 ppm) to avoid poisoning of the Pt-based

anodic catalysts [3, 4]. Among all available methods of hydrogen production, reforming of hydrocarbons (e.g. natural gas, C₂-C₄, ethanol, methanol, etc.) reveals better conditions against challenges like hydrogen storage [5-7]. Generally, methanol steam reforming (MSR) represents advantages of lower temperature operation (non C-C band); and moreover, CO

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consumption by water-gas shift reaction (as a side-reaction) without initial purification [5, 8-11]. Theoretically, this reaction is considered [8-10] as follows:



The process is totally endothermic, and in case of CO formation, because the WGS reaction is a moderately exothermic reaction, raising the temperature would improve undesirable reverse water-gas shift (RWGS) reaction [15-17]. To organize the related catalysts, the Cu-based catalysts and transition-metals-based catalysts (of 8th to 10th groups) have been frequently used in MSR, in which the former induce good activity and selectivity, and also lower stability [11-17]; while the latter show lower activity but promising thermal stability. To improve reactivity and stability of the Cu-based catalysts, various metals like Zn [16-23], Ce [15, 24-28], and Zr [14, 19, 21, 29-31] have been employed, while commercially, the CuZnAl catalyst is mainly used for MSR process [16, 32-34]. During the reaction some CO is produced which should be removed in a purification step for fuel cell processing system. In this study, various ratios of nanostructured Cu/Zn/Fe mixed oxides catalysts have been prepared by coprecipitation method for MSR reaction. The main purpose of this research is to present

new catalysts which have an acceptable selectivity and nearly full conversion of methanol and also high thermal stability during MSR reaction.

2. Experimental

2.1. Catalyst preparation

The co-precipitation method was used to synthesize Cu/Zn/Al and Cu/Zn/Fe mixed oxides with different compositions. No surfactant or modifier was used during synthesis. The metal nitrates of Cu(NO₃)₂.3H₂O (Luba Chemie, 99.9 %), Fe(NO₃)₃.9H₂O (Luba Chemie, 99.9 %) and Zn(NO₃)₂.4H₂O (Luba Chemie, 99.9 %) were employed for Cu/Fe and Cu/Zn/Fe preparation. The nitrates were dissolved into the water until they reached a solution of 0.2 M. They were added into a beaker containing heated water (200 ml, 80 °C) on stirrer at 350 rpm. The precipitating agent of Na₂CO₃ (0.5 M) was used to adjust pH around 7. The obtained precipitate was aged at 60 °C for 2 h under strong stirring. Afterward, the solids were filtered and washed with warm deionized water several times and dried at 110 °C for 12 h. Then, the dried powder was calcined in a furnace at 350 °C for 4 h. The obtained powder was shaped to a disk, pressed, crushed and sieved by a screen mesh No. 40–60. Table 1 illustrates the code and weight ratios of each catalyst.

2.2. Catalyst Characterization

Various tests have been performed to characterize the prepared catalysts properties. The Brunauer–Emmett–Teller (BET) method was used to measure the surface area of the prepared catalysts. The X-ray diffraction

(XRD) patterns were recorded on a Philips X'pert Pro MPD model X-ray diffractometer using Cu K α monochromatized radiation as the X-ray source. The diffractograms were recorded in the 2 θ range of 5- 70°. The spectra of catalyst were collected after calcination. The particle size could be estimated from the widths of the XRD peaks using the Scherer's equation. To probe and study the reduction capability of the prepared catalysts at various

conditions, the temperature-programmed reduction (TPR) analysis was carried out by using an automatic device (Micromeritics Chemisorb 2750) equipped with a thermal conductivity detector (TCD). The synthesized catalysts (100 mg) reduced via thermal rate of 10 °C/min by a stream containing 10 % H₂ in Ar with flowrate of 30 ml/min. Before the analysis, the samples were heated in a N₂ atmosphere at 350 °C for 3 h.

Table 1

Compositions and abbreviations of the synthesized catalysts.

Catalyst (%)	Composition (wt %)				Code
	CuO	ZnO	Al ₂ O ₃	Fe ₂ O ₃	
30CuO/70Al ₂ O ₃	30	-	70	-	30CA
30CuO/70Fe ₂ O ₃	30	-	-	70	30CF
40CuO/55ZnO/5 Fe ₂ O ₃	40	55	-	5	40CZ5F
40CuO/50ZnO/10 Fe ₂ O ₃	40	50	-	10	40CZ10F
40CuO/45ZnO/15 Fe ₂ O ₃	40	45	-	15	40CZ15F
40CuO/40ZnO/20 Fe ₂ O ₃	40	40	-	20	40CZ20F
40CuO/30ZnO/30 Fe ₂ O ₃	40	30	-	30	40CZ30F
45CuO/50ZnO/5 Fe ₂ O ₃	45	50	-	5	45CZ5F
55CuO/40ZnO/5 Fe ₂ O ₃	55	40	-	5	55CZ5F

2.3. Catalytic reaction

Methanol steam reforming reaction was carried out within a quartz tube-shaped reactor (8 mm inner diameter). The reactor was placed into a cylindrical furnace equipped with a temperature indicator and controller (PX9, Hanyoung, Korea). A K-type thermocouple was attached to the reactor to control the reaction temperature. Prior to the reaction, each case reduced via a stream containing 40 cm³/min of H₂ and Ar with equal volumetric ratio at atmospheric pressure

and temperature of 300 °C for 2 h. The output gases were analyzed by a gas chromatograph (GC, Shimadzu-8A Hysep Q column), with a TCD. For all experiments, 500 mg catalyst was packed into the reactor and Ar was used as carrier gas. The catalyst performance was examined at 230-270 °C and atmospheric pressure. The steam to carbon ratio (S/C) and gas hourly space velocity (GHSV) were fixed at 1.3 and 18000 h⁻¹, respectively.

The methanol conversion and CO selectivity are defined as the following equations [12]:

$$X(\%) = \frac{F_{in,MeOH} - F_{out,MeOH}}{F_{in,MeOH}} \times 100 \quad (4)$$

$$S_{CO}(\%) = \frac{F_{CO}}{F_{CO} + F_{CO_2}} \times 100 \quad (5)$$

Where, F (mol/s) denotes molar rate for each species.

3. Results and discussion

Figure 1 shows the XRD patterns of the different synthesized catalysts calcined at 350 °C in range of $2\theta = 10 - 80^\circ$. The peaks at $2\theta = 31.75^\circ, 34.53^\circ, 36.06^\circ, 47.77^\circ, 50.66^\circ, 62.73^\circ$ and 67.94° are related to ZnO (hexagonal phase of ZnO, JCPDS 01-080-1268). The peak at $2\theta = 38.65^\circ$ is related to CuO crystallinity (monoclinic phase of CuO, JCPDS 01-080-1268). The co-precipitation method usually results in low intensity peaks [35]. The crystalline sizes of the catalysts were estimated by Scherer's equation in which crystalline size of 12, 10.8 and 7.6 nm were achieved for 40CZ10F, 45CZ5F and 40CZ20F respectively. It is found that the crystalline size increased with rise in Zn loading. For further characterization of inner architectures

of the CuZnFe catalyst and texture properties, N_2 adsorption/desorption isotherms were measured. The pore size distribution based on the desorption branch of the nitrogen isotherm was calculated using Barrett-Joyner-Halenda (BJH) method. All isotherms could be classified as type III isotherm in the Brunauer classification [36], which does not restrict adsorption at higher relative pressures. This type is usually found in solid structures containing holes and aggregated/nonaggregated cubic or plane-like particles with unequal shapes and sizes (Fig. 2(a)). Regarding the IUPAC classification, the detected loops are signed as type H3 loops representing mesoporous structure. The results show that Fe addition coprecipitated with Cu reveals less BET than that using Al, as illustrated in Table 2. Considering Fig. 2(b), it could be found that all prepared samples possess mesostructures, and besides, the Zn-containing catalysts reveal macrohole structure.

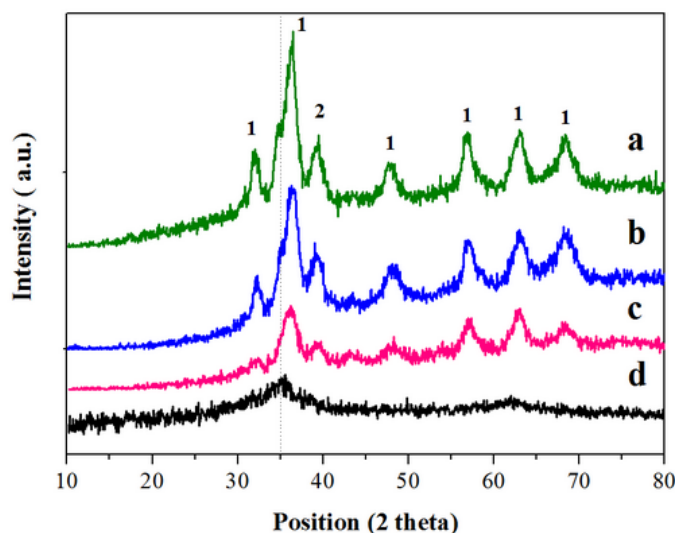
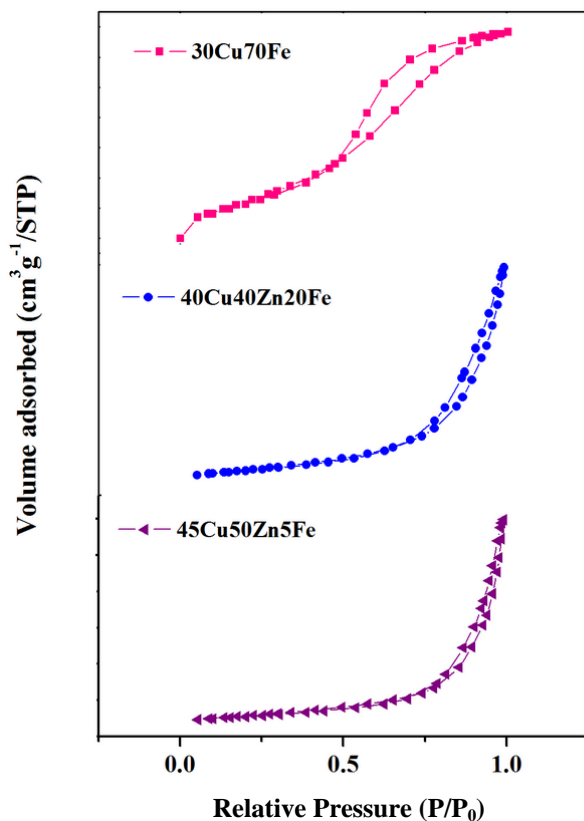
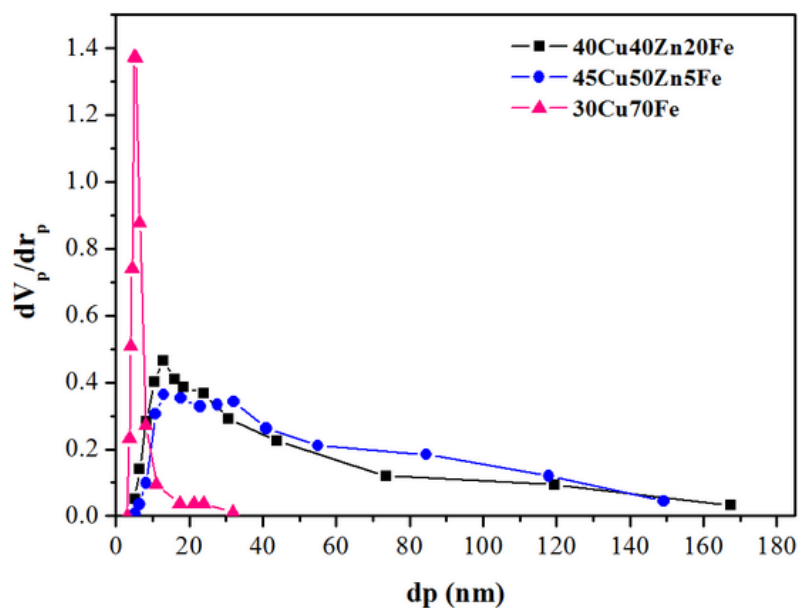


Figure 1. XRD patterns of the CuO/ZnO/Fe₂O₃ catalysts. (a) 40CZ10F (b) 45CZ5F (c) 40CZ20F (d) 30CF.



(a)



(b)

Figure 2. (a) Absorption and desorption isotherms plot for CuO/ZnO/Fe₂O₃ catalysts (b) CuO/ZnO/Fe₂O₃ catalyst pore size distribution curve with various Cu/Zn/Fe weight ratios.

Table 2

BET surface, pore volume and average sizes for Cu/Al, Cu/Fe and Cu/Zn/Fe catalysts.

Catalyst	BET (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
30CF	177	0.27	6.10
40CZ20F	84	0.34	15.98
45CZ5F	66	0.31	18.60
30CA	253	0.98	15.51

TPR diagram related to the 40CZ20F and 45CZ5F samples is shown in Fig. 3. The first peak is related to the CuO reduction to metallic Cu⁰. It is obvious that more Cu loading consumes more H₂ and slightly shifts its reduction to higher temperatures to completely reduce into Cu. Moreover, increase in Fe loading accelerates CuO reduction. In addition, the Fe addition improves catalyst stability and also reducibility because Fe is immiscible with Cu [37, 38]. The second peak is related to the Zn-Fe interaction or CuFe₂O₄ which increase in Fe loading, conducting the reduction toward higher temperatures. Figure 4 shows SEM images of 45CZ5F in which irregular blade shape morphology consisting of plates in different size is obvious.

Prior to Zn loading, the 30CF and 30CA were examined, the latter showed about 8 % higher methanol conversion as illustrated in the Table 3. To assess the ZnO role precipitated into the Cu and Fe oxides, it was added to improve performance of Cu-Fe catalyst as stated before [4]. Figure 5 shows the MSR performance for different loading of Zn, as can be seen the methanol conversion is

raised via increase in temperature. It ranges from 40.29 to 67.52 % for 40CZ5F, as the temperature is changed from 230 to 270 °C. More loading of Fe to 20 wt % empowers the methanol conversion and simultaneously weakens CO formation. The Fe loading higher than 20 wt % significantly decreases the methanol conversion and slightly improves CO production. The Cu surface area is raised with further Fe loading, although the conversion might be lower [37]. The 40CZ20F found as optimal case, reveals maximum conversion of 89.7 % with CO selectivity of 0.65 % at 270 °C.

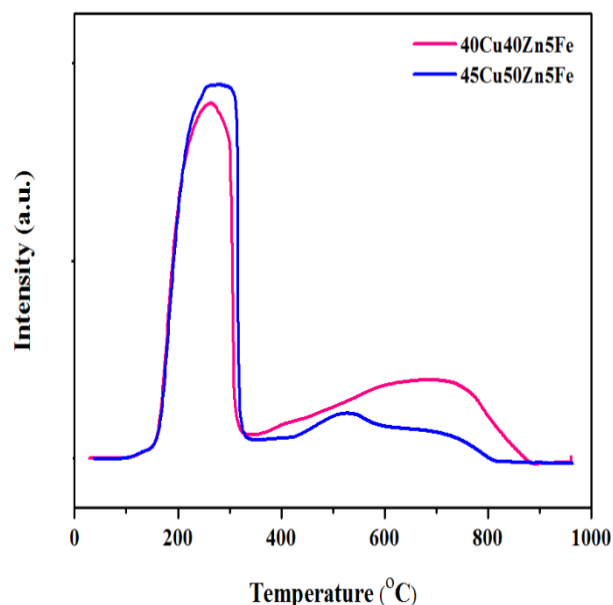


Figure 3. Temperature programmed reduction (TPR) profiles of the fresh CuO/ZnO/Fe₂O₃ catalyst. 45Cu50Zn5Fe (solid line) and 40Cu40Zn20Fe (dotted line).

To investigate the reason of enhancing methanol conversion and CO production with the CuZnFe catalyst, the Fe loading was kept constant in its minimum amount (5 wt %) and the Cu/Zn ratios were examined.

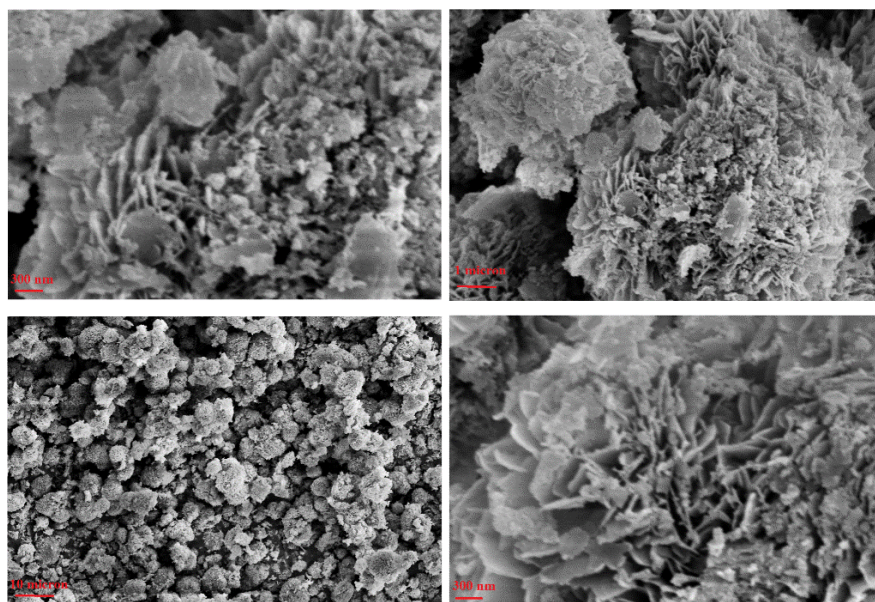


Figure 4. Scanning electron micrographs (SEM) image of the fresh 45Cu50Zn5Fe catalyst at different magnification.

Table 3

Methanol conversion and product selectivity for Cu/Al and Cu/Fe catalysts.

Catalyst	Synthesis method	Temperature (°C)	MeOH conversion (%)	CO ₂ selectivity (%)	CO selectivity (%)
30CA	CP ^a	270	70	99.37	0.63
30CF	CP	270	62	99.02	0.98
40CZ5F	CP	270	67.5	99.08	0.92
40CZ10F	CP	270	72.7	99.17	0.83
40CZ15F	CP	270	77	99.20	0.80
40CZ20F	CP	270	89.7	99.35	0.65
40CZ30F	CP	270	77.8	99.05	0.95
45CZ5F	CP	270	98.4	99.22	0.78
55CZ5F	CP	270	81.62	98.80	1.2

a: Co-precipitation

As displayed in Fig. 6, considering the Cu/Zn ratios of 0.7, 0.9, and 1.4 for CuZnFe, it is observed that the ratio of 0.9 induces better performance while the conversion is decreased at lower and higher ratios of 0.9. In case of CO

selectivity, better performance is observed. It could be concluded that using Cu/Zn ratio of 0.9 and lower amount of Fe (5 wt %) causes higher methanol conversion.

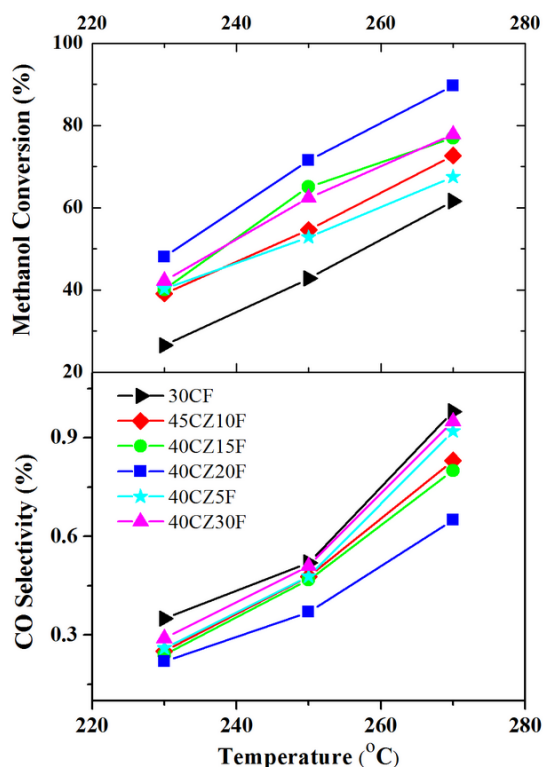


Figure 5. Steam reforming of methanol over CuO/ZnO/Fe₂O₃ catalysts with various Zn/Fe ratios. S/C = 1.3, GHSV = 18000 h⁻¹, reaction temperature = 230-270 °C.

Table 4 illustrates an overview to compare the prepared catalyst of 45CZ5F performance against some commercial and prepared cases in other literatures. As can be seen, the prepared catalyst of 45CZ5F shows higher methanol conversion than that of commercial one at 270 °C. In case of CO formation the results could be acceptable although they do not completely guarantee the PEMFC requirements.

3.1. Optimal conditions of 45CZ5F catalyst

Five S/C ratios of 0.7, 1.0, 1.3, 1.5, and 2.0 were selected to assess feedstock effect over 45CZ5F catalyst.

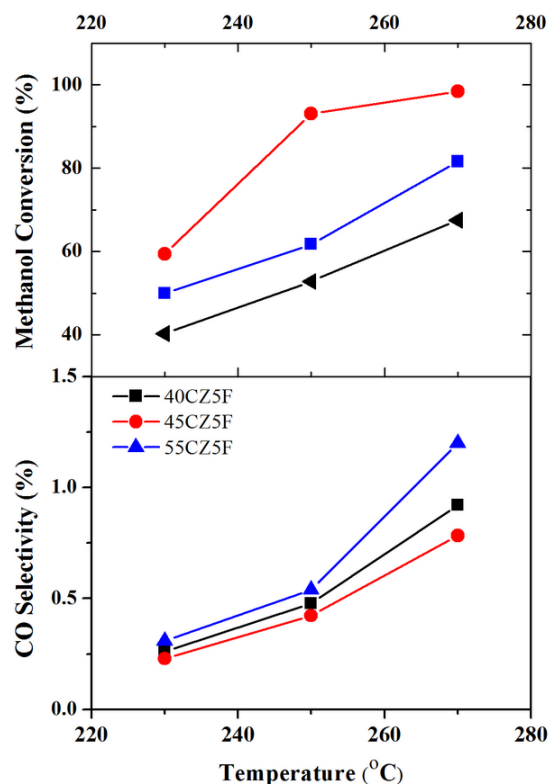


Figure 6. Steam reforming of methanol over CuO/ZnO/Fe₂O₃ catalysts with various Cu/Zn ratios. S/C = 1.3, GHSV = 18000 h⁻¹, reaction temperature = 230-270 °C.

As shown in Fig. 7, by increase in the ratio to 1.3, the methanol conversion increased while the ratios higher than that lower the methanol conversion. In case of CO selectivity, the S/C ratio facilitates disappearing CO in the output. According to the results, higher S/C is more favorable to reduce the CO content. Eq. (1) shows that the S/C of 1.0 will be stoichiometrically optimal for MSR. However, according to Eq. (1) and (3), the excess steam develops methanol conversion and decreases the CO content through conducting the water gas shift equilibrium rightward. Moreover, the system will be more cost-effective with lower steam

due to the heating problems. The gas hourly space velocities (GHSVs) of 9000, 12000, 18000, 27000 and 36000 h⁻¹ were adjusted to 500 mg of 45CZ5F catalyst. As displayed in Fig. 8, it is obvious that the methanol conversion reduced by increases in GHSV. It is the result of the lower contact time of the

reactants on the catalyst sites. On the contrary, the CO selectivity diagram demonstrates that increase in GHSV results in less CO generation. Figure 9 shows the stability performance, in which the methanol conversion and CO selectivity remained constant during 17 h at 270 °C.

Table 4

Performance assessment of the Cu-based catalysts for MSR.

Catalyst	Synthesis method	Temperature (°C)	MeOH conversion (%)	CO selectivity (%)	Reference
30CA	CP ^a	270	70	0.63	This study
30CF	CP	270	62	0.98	This study
45CZ5F	CP	270	98.4	0.78	This study
Cu/ZnO	-	260	75	-	[39]
Cu/ZnO/Al ₂ O ₃	-	260	79	0.62	[39]
Cu/ZnO/Al ₂ O ₃ ^b	-	270	59	-	[10]
Cu/ZnO/Al ₂ O ₃	-	270	89.2	0.92	[10]
Cu/Al ₂ O ₃	-	260	22	0.4	[40]
Cu/ZnO/Al ₂ O ₃	CP	270	78	0.6	[21]
Cu/ZnO/Al ₂ O ₃	CP	270	84	-	[41]

a: Co-precipitation b: Commercial

4. Conclusions

Nanostructured CuZnFe catalysts were synthesized by coprecipitation method and successfully catalyzed in MSR reaction. The case of 30CF revealed lower methanol conversion than 30CA. Based on the Fe optimization, increase in this loading to 20 wt % resulted in higher methanol conversion and lower CO selectivity, simultaneously. Afterwards, further Cu loading from 40 to 45 wt % improved methanol conversion while with more loading a slight decrease was observed. The XRD patterns showed a nanocrystalized structure and also based on

the SEM images, nonregular plate shape morphology was found. Employing Fe into the CuZnFe structure decreased the BET surface area. The 40CZ5F possessed the highest methanol conversion compared to the other cases and also its activity was kept constant during 17 h time on stream. To optimize the operating conditions, S/C and GHSV were assessed so that the former showed that increase in the ratio to 1.3 that improved methanol conversion and further than that lowered the conversion while the CO selectivity continuously decreased. Moreover, the methanol conversion decreased as the

GHSV increased owing to the contact time of the reactants on the active sites.

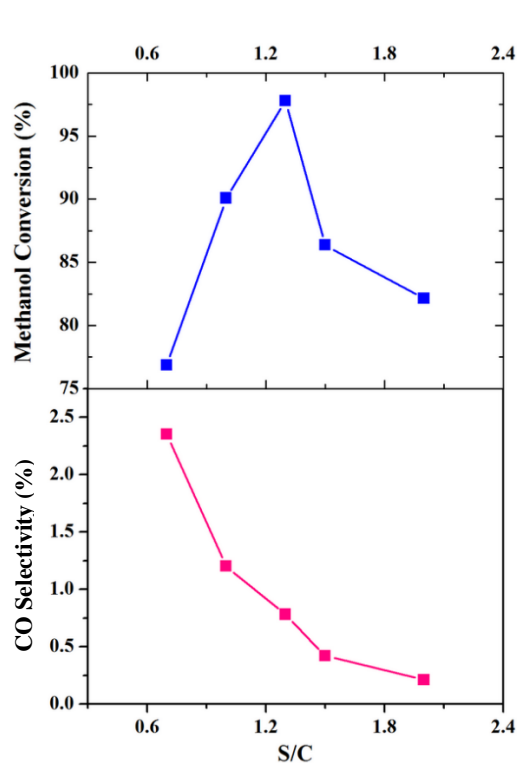


Figure 7. Methanol conversion and CO selectivity versus S/C molar feed ratio at reaction temperature=270 °C and GHSV=18000 h⁻¹ for 45CuZn5Fe catalyst.

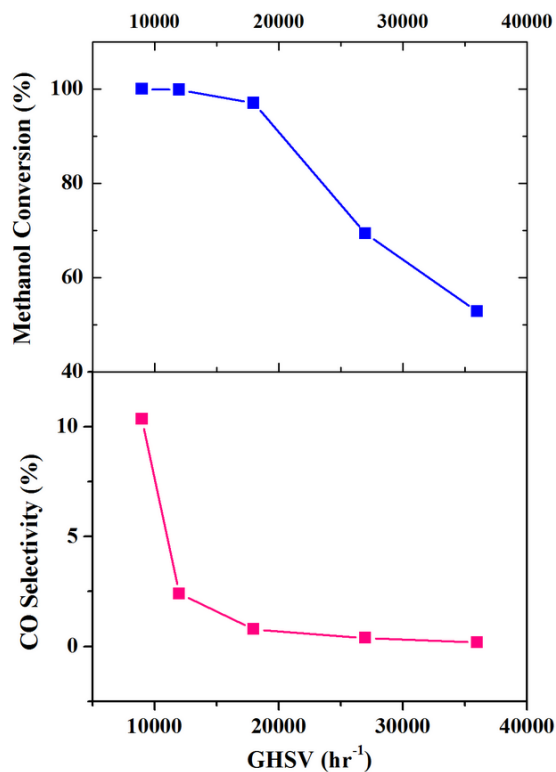


Figure 8. Methanol conversion and CO selectivity as a function of the GHSV at reaction temperature = 270 °C and S/C = 1.3 for 45CuZn5Fe catalyst.

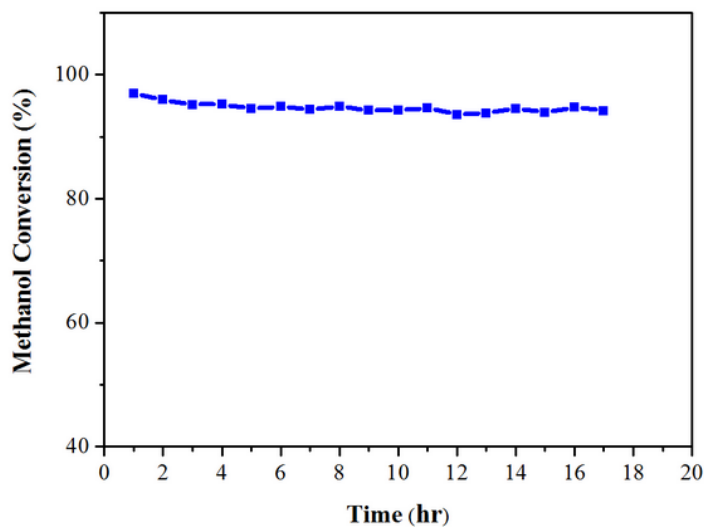


Figure 9. Methanol conversion and CO selectivity versus time on stream in steam reforming of methanol (MSR) at reaction temperature = 270 °C and GHSV = 18000 h⁻¹ and S/C = 1.3 for 45CuZn5Fe catalyst.

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