

# EFFECTS OF PREPARATION OF Cu/Zn OVER Al<sub>2</sub>O<sub>3</sub> CATALYSTS FOR HYDROGEN PRODUCTION FROM METHANOL REFORMING

Suparoek Henpraserttae<sup>1,2</sup> and Pisanu Toochinda<sup>1\*</sup>

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## Abstract

A novel catalyst for hydrogen production from the catalytic methanol reforming process could play an important role in hydrogen production to be used as a feed for a fuel cell. This study focuses on the preparation methods of active Cu/Zn based catalysts with and without urea by incipient wetness impregnations to lower the metal loading and catalyst cost. The catalytic methanol reforming was studied in a fixed-bed reactor under mild conditions and a reaction temperature range of 453 and 523 K in order to lower energy costs. The activity in the hydrogen production of the impregnated catalysts and a commercial catalyst was analyzed by gas chromatography and compared in terms of hydrogen production yield. The catalysts were also characterized by XRD and SEM in order to identify the physical and chemical properties of the catalysts. The data show that the activity in hydrogen production from the catalysts with urea is higher than that of the catalysts without urea. The impregnated catalysts could exhibit activity at as low a temperature as 453 K which indicates the possibility of lowering the reaction temperature for the methanol reforming process. The Cu/Zn catalysts prepared by incipient wetness impregnation over Al<sub>2</sub>O<sub>3</sub> with urea could exhibit high activity about 28% H<sub>2</sub> yield with efficiency about 97% compared with the commercial catalyst. The impregnated catalysts could be alternative catalysts for hydrogen production from methanol reforming with a lower cost of the catalyst compared with the co-precipitation method used in a commercial one.

**Keywords:** Methanol reforming, Hydrogen production, Cu/Zn based catalysts, Incipient wetness impregnations

## Introduction

The growing world population has had a large effect on the demand for energy. To date, fossil fuels have been used as the main energy sources to support such demand. Unfortunately, fossil fuel reserves are expected to last no longer than 50-100 years. The shortage of energy is thus

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<sup>1</sup> School of Bio-Chemical Engineering and Technology, Sirindhorn International Institute of Technology, Thammasat University, P.O. Box 22, Pathumthani, Thailand 12121. E-mail: pisanu@siit.tu.ac.th  
Tel: +66-2-986-9009 ext 2305

<sup>2</sup> National Metal and Materials Technology Center, National Science and Technology Development Agency, Klong-I, Klong-luang, Pathumthani, Thailand 12120

\* Corresponding author

becoming an important problem for mankind, prompting worldwide searches for alternative energy (Shafiee and Topal, 2007).

One interesting alternative energy is energy from hydrogen feeding to a fuel cell creating electricity. A fuel cell unit generates electrical energy from an electrochemical reaction of hydrogen with oxygen, yielding an environmentally benign by product, water (Zhang *et al.*, 2008; Kulikovskiy, 2008; Sholkapper *et al.*, 2008). The hydrogen fuel cell is claimed as an alternative energy resource, with high efficiency compared with conventional internal combustion engines, to replace fossil fuel (Edwards *et al.*, 1998; Bowers *et al.*, 2007).

Hydrogen could be produced from the reforming reaction of hydrocarbons such as methane, ethanol, methanol, etc (Alessandra and Elisabete, 2006; Papavasiliou *et al.*, 2007; Campos-Skrobot *et al.*, 2008). The methane reforming reaction requires a huge amount of energy, 973-1273 K (Zhou *et al.*, 2008; Xu *et al.*, 2008) while the ethanol has been used in various applications such as gasohol and food production. Methane and ethanol have been widely used as energy resources, so there is no need to spend significant amount of energy to convert methane and ethanol to be hydrogen. One of the attractive choices for the hydrogen production from the reforming reaction is methanol. Methanol is considered as low cost, as having a low boiling point, low reforming temperature, high energy density, high H/C ratio and as being easily stored. This study focuses on methanol steam reforming reaction to produce hydrogen for a fuel cell. The reaction is shown as follows (Patel and Pant, 2007; Shishido *et al.*, 2007; Basile *et al.*, 2008). Steam reforming:



$$\Delta H^0 = 49.5 \text{ kJ/mol}$$

Hydrogen could be produced from a reaction of methanol and water. This reaction provides the highest hydrogen production among other various reforming reactions. Unfortunately,

the process still requires a huge amount of energy in order to produce a high yield of hydrogen. This is a major drawback of hydrogen production from the reforming reaction. The Cu-Zn based catalysts require a high operation temperature of 523-573 K to produce the effective hydrogen yield (Shishido *et al.*, 2004; Yao *et al.*, 2006; Patel and Pant, 2007). Ironically, in order to operate a hydrogen fuel cell, the hydrogen could be obtained from the process with a high cost of energy expenditure. Most of the Cu-Zn based catalysts and commercial catalysts were prepared by using Cu and Zn contents as high as 60-90 weight percent by the co-precipitation method to produce the high yield of hydrogen (Patel and Pant, 2007; Shishido *et al.*, 2007). Literatures have been reported on the use of urea in precipitation of Cu/Zn-based catalysts could exhibit higher activity of methanol reforming than those of the catalysts prepared by precipitation without using urea. The addition of urea allows the formation of precipitates to have better homogeneity of metal cation distribution in the solution and could yield high surface area precipitates which composed by small pieces of metals stick together in spherical shape (Murcia-Mascarós *et al.*, 2001; Shishido *et al.*, 2004; Turco *et al.*, 2004; Shishido *et al.*, 2007).

The incipient wetness impregnation over porous materials have been widely used for many catalyst preparations due to the ease of method and small amount of active metal content relative to other catalyst preparation methods which could lower the cost of catalyst production (Patel and Pant, 2006). The impregnation of Cu and Zn with urea on the support such as alumina might be able to exhibit a high activity of hydrogen production without using a high metal loading on the catalyst.

The objective of this work is to study the performance of various metal contents impregnated on  $\text{Al}_2\text{O}_3$  for the methanol reforming reaction. This study also focus on the Cu-Zn based catalyst with and without urea impregnated on  $\text{Al}_2\text{O}_3$  to study the catalytic performance of the methanol reforming

reaction. The performances of the catalysts are compared with the performance of a commercial one. The results of this study could lead to a better understanding of the role of catalyst preparation in order to develop novel catalysts for hydrogen production from the methanol reforming process.

## Experimental

### Catalyst Preparation

Cu-Zn based catalysts were prepared with urea (CZU) and without urea (CZ) followed by impregnation over  $\text{Al}_2\text{O}_3$ . The catalyst prepared with urea (CZU) was synthesized by impregnating the aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (99%, Fluka) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99%, Fluka) with the addition of urea (99%, Carlo Erba) over  $\text{Al}_2\text{O}_3$  (98%, Riedel-de Haën). The catalyst prepared without urea was synthesized by impregnating the aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  over  $\text{Al}_2\text{O}_3$ . The impregnated samples were dried in air at 373 K for 12 h and then calcined in air at 573 K for 3 h. The commercial catalyst used for comparison was Cu/Zn/ $\text{Al}_2\text{O}_3$  from Süd-Chemie AG (München, Germany). The compositions of the catalysts synthesized and their abbreviations are shown in Table 1.

### Methanol Reforming Reaction in Tubular Reactor

The methanol steam reforming reaction

for the hydrogen production was studied on the prepared catalysts in a stainless steel tubular reactor which has an inside diameter of 1 cm. Two grams of catalyst were packed between quartz wool in the tubular reactor. The catalyst was reduced with 50 ml/min of 10%  $\text{H}_2$  :  $\text{N}_2$  balanced at 453 K for 1 h prior to the methanol reforming reaction test. The reactor was flushed with 50 ml/min  $\text{N}_2$  flow at 453 K for 30 min to get rid of adsorbed hydrogen from the reduction process. The mixture of methanol and water solution was loaded into a saturator which was heated at 333 K. The compositions of methanol and water in the liquid phase are 0.125:0.875 molar ratio. The composition of solution was calculated by the Aspen Plus simulation program (Aspen Technology Inc., Burlington, Mass., USA) to ensure that the composition of the mixture in the vapor phase is a 1:1 molar ratio at the outlet from the saturator. The vapor of the mixture in the saturator was carried at 20 ml/min  $\text{N}_2$  into the reactor at 453 K and 523 K in a continuous system. Therefore, the space time of the packed bed reactor in a continuous mode was about 6 second. The product was collected and the production of hydrogen was determined via gas chromatography (GC).

### Analysis Section

A Perkin Elmer (Waltham, Mass., USA) Autosystem XL gas chromatograph with Porapak Q column (Supleco, Bellefonte, PA, USA) coupled with a thermal conductivity

**Table 1. The compositions of Cu-Zn catalysts for methanol reforming**

Catalyst	Composition (Cu/Zn/ $\text{Al}_2\text{O}_3$ ) (% wt)	Urea (mole/mole <sub>Cu</sub> )
10CZ	5 / 5 / 90	0
10CZU1	5 / 5 / 90	1
10CZU2	5 / 5 / 90	2
20CZ	10 / 10 / 80	0
20CZU1	10 / 10 / 80	1
20CZU2	10 / 10 / 80	2
Commercial	40 / 30 / 30	0

detector (TCD) was used to determine the amount of hydrogen production. The GC was affixed to a computer for automatic determination of peak areas which could be converted to concentration.

The surfaces of the catalysts were inspected by a scanning electron microscope (SEM, JEOL JSM-5410, Jeol Inc., Tokyo, Japan). The elemental composition of the catalyst surface was determined by energy dispersive spectrometry (EDS, Oxford) that was equipped with SEM.

The catalysts were characterized by the X-ray diffraction technique (XRD, JEOL JDX-3530, Jeol Inc., Tokyo, Japan) using Cu  $K_{\alpha 1}$  radiation,  $30^{\circ}$  -  $41^{\circ}$  2-theta,  $0.04^{\circ}$  step size, 0.5 sec step time. JADE software (Jade Software Corporation Ltd., Christchurch, New Zealand) was used to determine the crystallize size of the CuO and identify phases of the catalysts with the database of an X-ray diffractogram from the International Centre for Diffraction Data

(Newtown Square, PA, USA).

## Results and Discussion

### Activity of the Catalysts for Methanol Reforming

Hydrogen production from the methanol reforming reaction over various catalysts was investigated and the results are reported in Table 2. Percent  $H_2$  yields were calculated using the following equation;

$$\%H_2 \text{ yield} = \frac{1}{3} \frac{\text{mol of } H_2}{\text{mol of } CH_3OH \text{ fed}} \times 100$$

Table 2 shows that the higher metal loading on the catalysts leads to a higher activity of the catalyst which is indicated by the 20 wt% metal loading catalysts (20CZ, 20CZU1, 20CZU2) exhibiting an activity higher than those

**Table 2. Hydrogen production from methanol reforming over various catalysts at 453 K and 523K**

Cu-Zn-Al <sub>2</sub> O <sub>3</sub> Catalysts (Cu/Zn/Al <sub>2</sub> O <sub>3</sub> ) (% wt)		Temperature (K)	% H <sub>2</sub> yield	
10CZ	(5/5/90)	453	< 10	
10CZU1	(5/5/90)		< 10	
10CZU2	(5/5/90)		19	
20CZ	(10/10/80)		13	
20CZU1	(10/10/80)		17	
20CZU2	(10/10/80)		21	
Commercial	(40/30/30)		25	
10CZ	(5/5/90)		523	13
10CZU1	(5/5/90)			22
10CZU2	(5/5/90)	26		
20CZ	(10/10/80)	20		
20CZU1	(10/10/80)	25		
20CZU2	(10/10/80)	28		
Commercial	(40/30/30)	29		

of the 10 wt% metal loading catalysts (10CZ, 10CZU1, 10CZU2) at both 453 and 523 K. The data also show that the amount of urea affects the catalytic activity of the hydrogen production at both 10% and 20% metal loading which is indicated by the results of the higher CZU2 urea catalysts, which exhibit higher activity than that of the lower CZU1 urea catalysts at 453 and 523 K. Among all the catalysts in this study, the commercial catalyst exhibits the highest hydrogen yield but the Cu and Zn loading on the commercial catalyst (Cu/Zn/Al<sub>2</sub>O<sub>3</sub> : 40/30/30 wt%) is much higher than that of the impregnated catalysts in this study. The metal loading of the commercial catalyst is about 4 times higher than that of the 20CZU1 and 20CZU2 but the hydrogen yield of the commercial one is about 1.5 and 1.2 times respectively, at 453 K and only about 1.2 and 1.04 times respectively, at 523 K. From the results, even though the impregnated catalysts have much a lower metal loading, they still can exhibit a comparable hydrogen yield to the commercial catalyst. The results also indicate

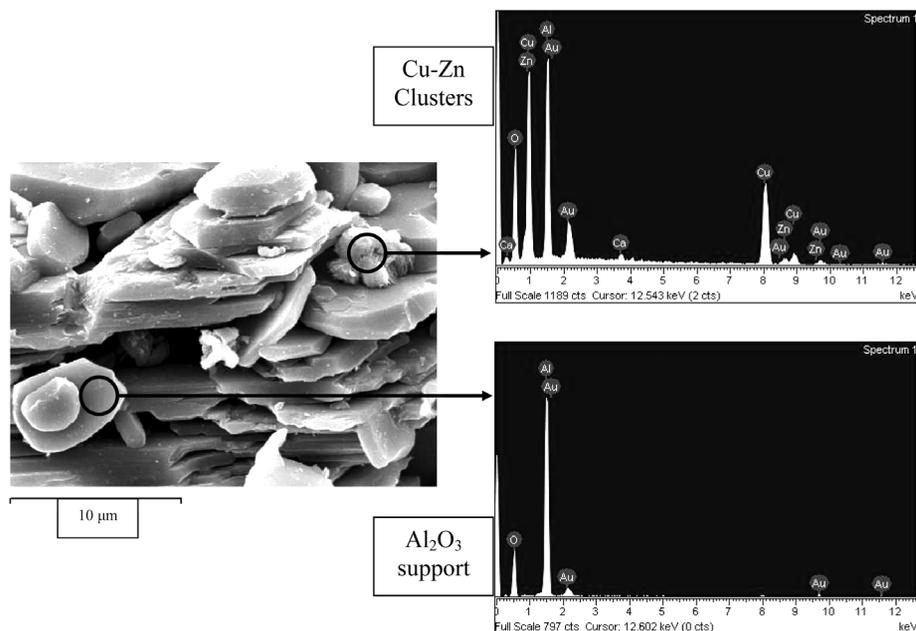
that the higher metal loading on the impregnated catalysts with urea could exhibit a high activity and be able to compete with the commercial one.

The lower metal loading and simple preparation method of the impregnated catalysts in this study could provide another choice of catalyst for methanol reforming with a lower cost of catalyst production compared with the conventional catalysts. This study also shows that the impregnated catalysts in this study could exhibit activity of hydrogen production at as low a temperature as 453 K which indicates the possibility of lowering the reaction temperature for the methanol reforming process.

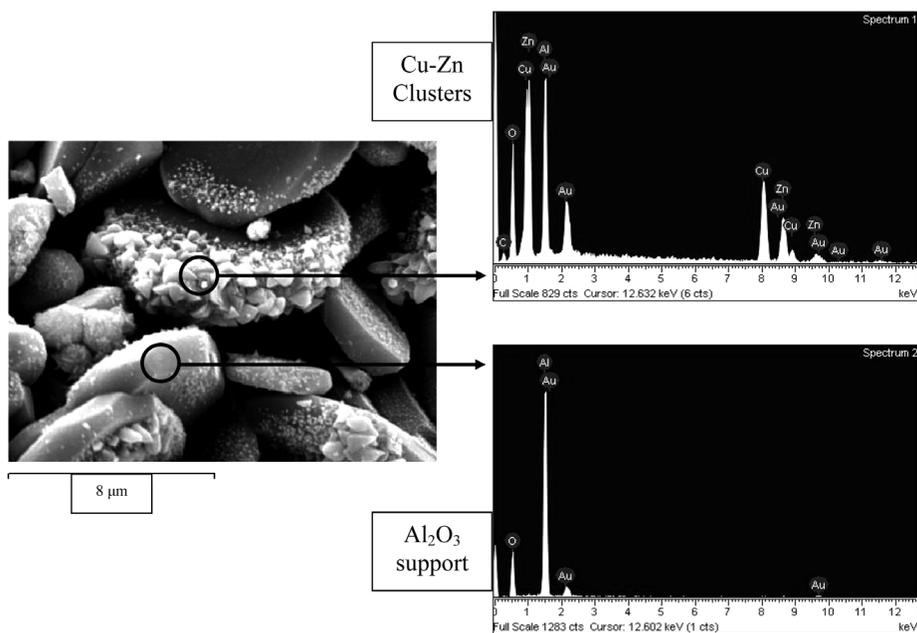
### Catalyst Characterization

The CZ-catalyst, CZU-catalyst, and commercial catalyst were characterized by scanning electron microscope with energy dispersive spectrometer (SEM-EDS) and X-ray diffractometer (XRD).

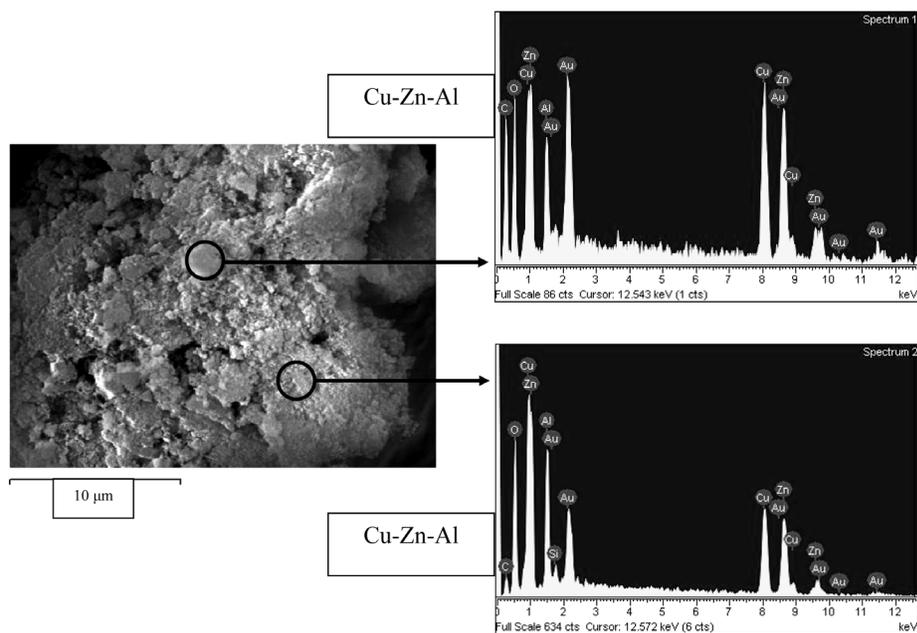
Figures 1 and 2 shows the SEM-EDS images of the CZ-catalyst and CZU-catalyst,



**Figure 1.** SEM image and EDS profiles of the impregnated Cu-Zn without urea over Al<sub>2</sub>O<sub>3</sub> catalyst for methanol reforming



**Figure 2.** SEM image and EDS profiles of the impregnated Cu-Zn with urea over Al<sub>2</sub>O<sub>3</sub> catalyst for methanol reforming



**Figure 3.** SEM image and EDS profiles of the commercial catalyst for methanol reforming

respectively. The images of these two types of catalysts show that the Cu and Zn deposited together in small clusters on the  $\text{Al}_2\text{O}_3$  surface. The EDS profiles indicate that the small clusters are composed of Cu and Zn located on the support which is Al. The SEM images also show that the sizes of Cu-Zn clusters on the catalysts with urea, CZU ( $H \approx 0.5\text{-}1.5 \mu\text{m}$ ), are much smaller than those of the catalysts without urea, CZ ( $H \approx 2\text{-}4 \mu\text{m}$ ). The addition of urea could improve the homogeneity of the Cu and Zn composition in the impregnated solution and allow the formation of smaller metal cluster size. The smaller metal clusters with the same metal loading could provide more surface area of the active sites for the reaction. The higher numbers of active sites on the catalysts with urea, CZU, exhibit a higher activity of hydrogen production than that of the catalysts without urea, CZ, in both 10wt% and 20wt% metal loadings.

Figure 3 shows the SEM-EDS image of the commercial catalyst. The image shows that the metals are mixed well throughout the entire catalyst without forming any separated metal clusters. The EDS profile shows that the catalyst surface is composed of Cu, Zn, and Al species.

Figure 4 shows the SEM images of catalysts with and without urea at the same metal loading (20 wt%). The SEM images of 20CZ (Figure 4(a)) shows the agglomeration of a large Cu-Zn cluster ( $\approx 5\text{-}10 \mu\text{m}$ ) over  $\text{Al}_2\text{O}_3$ . The distribution of metal clusters is not consistent throughout the surface of  $\text{Al}_2\text{O}_3$ . The SEM images of 20CZU1 (Figure 4(b)) shows smaller Cu-Zn clusters ( $\approx 2\text{-}6 \mu\text{m}$ ) and better dispersion of Cu-Zn clusters over  $\text{Al}_2\text{O}_3$  than that of 20CZ. The SEM images of 20CZU2 (Figure 4(c)) clearly show the smallest Cu-Zn clusters ( $\approx 0.2\text{-}1.0 \mu\text{m}$ ) among the catalysts and also the best distribution of Cu-Zn clusters throughout the surface of  $\text{Al}_2\text{O}_3$ . The images imply better dispersion of Cu-Zn clusters and more active sites on  $\text{Al}_2\text{O}_3$  of the 20CZU2 catalyst over other impregnated Cu-Zn catalysts. The SEM results also support the highest hydrogen yield from 20CZU2 among other impregnated Cu-Zn catalysts in this study, which could be explained by the smallest metal

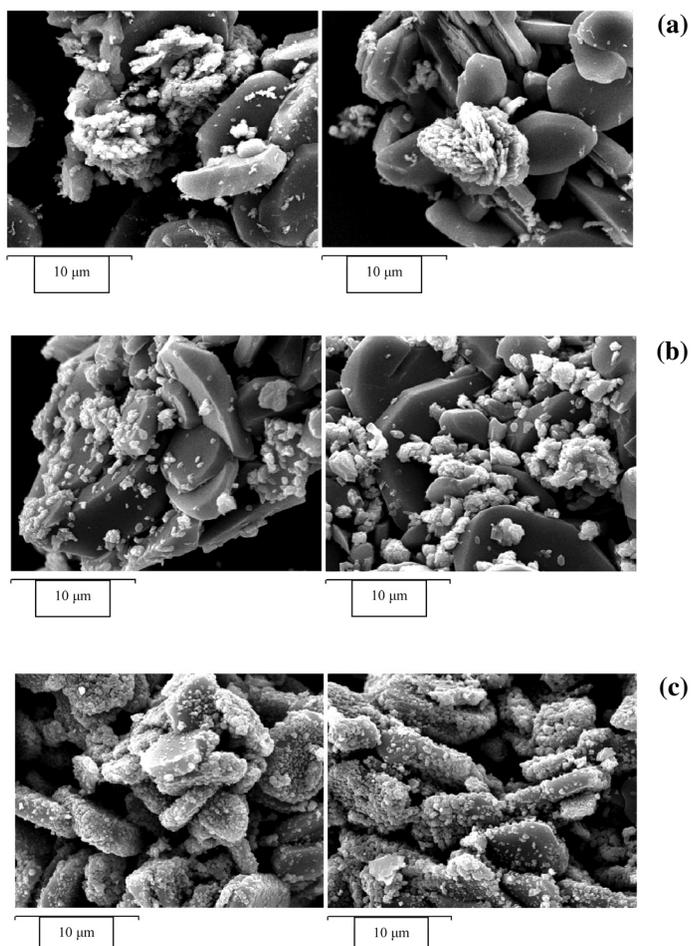
clusters and the best metal dispersion.

Figure 5 shows the X-ray diffractogram of the impregnated catalysts with and without urea and the commercial catalyst. The peak at  $2\theta$  equal to 31.8, 34, and 36.2 degrees indicates zinc oxide (Zincite, JCPDS No.: 36-1451). The copper oxide (Tenorite, JCPDS No.: 45-0937) peaks were observed at  $2\theta$  equal to 35.8 and 38.8 degrees. The diffractogram of the catalysts with and without urea exhibit a similar pattern to that of the commercial catalyst which ensures the same phases of Cu-Zn active sites on these catalysts. Table 3 shows the estimated crystallize size of CuO on the catalysts. Table 3 also shows that the higher moles of urea used in the preparation process yields the smaller crystallize size of CuO on the catalysts. The smaller crystallize size of CuO with the same metal loading could provide more active sites of CuO for the methanol reforming reaction which supports the results from the activity of the catalysts for the hydrogen production.

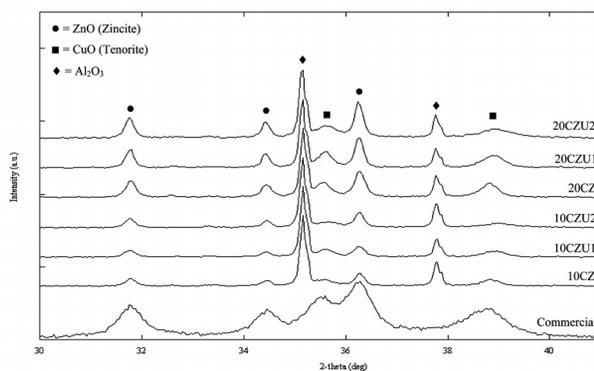
## Conclusions

The study shows that a higher metal loading on the catalyst leads to a higher activity of the catalyst which results in a higher hydrogen yield for the 20 wt% metal loading catalysts than for the 10 wt% metal loading catalysts. The impregnated Cu-Zn catalysts on  $\text{Al}_2\text{O}_3$  with urea exhibit a higher activity than those of the catalysts without urea.

The commercial catalyst has the highest hydrogen yield but also contains much higher Cu and Zn contents than the impregnated catalysts with and without urea. The hydrogen yield of the commercial catalyst is only about 1.2 and 1.04 times higher while the metal loading is about 4 times higher than those of the 20CZU1 and 20CZU2 catalysts at 523 K. Although, the impregnated catalysts have a much lower metal loading, they still can give a comparable hydrogen yield. The SEM-EDS images show that the Cu-Zn is deposited as a cluster over alumina. The SEM images also show that the amount of urea used in the preparation process plays an important role in the size of metal clusters and the dispersion of metal



**Figure 4.** SEM images of the impregnated Cu-Zn with and without urea over Al<sub>2</sub>O<sub>3</sub> catalyst for methanol reforming, (a) 20CZ, (b) 20CZU1 and (c) 20CZU2



**Figure 5.** X-ray diffractogram of the impregnated catalysts and the commercial catalyst for methanol reforming

**Table 3. Estimated crystallize size of CuO**

Sample	Estimated crystallize size of CuO <sup>a</sup>
	(nm)
10CZ	28
10CZU1	21
10CZU2	14
20CZ	29
20CZU1	22
20CZU2	14
Commercial	10

<sup>a</sup> determined by XRD using peak at 2-theta equal to 38.8°

clusters over Al<sub>2</sub>O<sub>3</sub>. The good dispersion of the small metal clusters over Al<sub>2</sub>O<sub>3</sub> results in a higher activity of hydrogen production. The crystallize size of CuO determined via XRD could confirm that the size of the CuO crystal depends on the amount of urea used in the preparation process. The study also shows that the methanol reforming reaction could be carried out at as low a temperature as 453 K which could save a lot of energy expenditure.

The production cost of the catalysts could be lower due to the ease of the preparation process and lower metal loading compared with the commercial catalyst. The proper metal loading of Cu-Zn with urea impregnated on the high surface area support could enhance the reaction activity and lower the operation temperature. The results of this study could lead to the development of the novel catalyst for hydrogen production from the methanol reforming process.

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### References

- Alessandra, F.L. and Elisabete M.A. (2006). Cobalt catalysts prepared from hydrotalcite precursors and tested in methane steam reforming. *J. Power Sources*, 159:667–672.
- Basile, A., Parmaliana, A., Tosti, S., Iulianelli, A., Gallucci, F., Espro, C., and Spooen, J. (2008). Hydrogen production by methanol steam reforming carried out in membrane reactor on Cu/Zn/Mg-based catalyst. *Catal. Today*, 137:17-22.
- Bowers, B.J., Zhao, J.L., Ruffo, M., Khan, R., Dattatraya, D., Dushman, N., Beziat, J.C., and Boudjemaa, F. (2007). Onboard fuel processor for PEM fuel cell vehicles. *Int. J. Hydrogen Energy*, 32:1,437-1,442.
- Campos Skrobot, F.C., Rizzo Domingues, R.C.P., Fernandes Machado, N.R.C., and Cantão, M.P. (2008). Novel zeolite-supported rhodium catalysts for ethanol steam reforming. *J. Power Sources* 183:713-716.
- Edwards, N., Ellis, S.R., Frost, J.C., Golunski, S.E., Keulen, A.N.J., Lindewald, N.G., and Reinkingh, J.G. (1998). On-board hydrogen generation for transportation applications: the HotSpot methanol processor. *J. Power Sources*, 71:123–128.
- Kulikovsky, A.A. (2008). Direct methanol–

- hydrogen fuel cell: The mechanism of functioning. *Electrochem. Commun.*, 10:1,415-1,418.
- Murcia-Mascarós, S., Navarro, R.M., Gómez-Sainero, L., Constantino, U., Nocchetti, M., and Fierro, J.L.G. (2001). Oxidative methanol reforming reactions on CuZnAl catalysts derived from hydrotalcite-like precursors. *J. Catal.*, 198:338-347.
- Papavasiliou, J., Avgouropoulos, G., and Ioannides, T. (2007). Effect of dopants on the performance of CuO–CeO<sub>2</sub> catalysts in methanol steam reforming. *Appl. Catal. B*, 69:226–234.
- Patel, S. and Pant, K.K. (2006). Activity and stability enhancement of copper-alumina catalysts using cerium and zinc promoters for the selective production of hydrogen via steam reforming of methanol. *J. Power Sources*, 159:139–143.
- Patel, S. and Pant, K.K. (2007). Selective production of hydrogen via oxidative steam reforming of methanol using Cu–Zn–Ce–Al oxide catalysts. *Chem. Eng. Sci.*, 62:5,436–5,443.
- Shafiee, S. and Topal, E. (2007). An econometrics view of worldwide fossil fuel consumption and the role of US. *Energy Policy*, 36:775–786.
- Shishido, T., Yamamoto, Y., Morioka, H., Takaki, K., and Takehira, K. (2004). Active Cu/ZnO and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by homogeneous precipitation method in steam reforming of methanol. *Appl. Catal. A*, 263: 249–253.
- Shishido, T., Yamamoto, Y., Morioka, H., and Takehira, K. (2007). Production of hydrogen from methanol over Cu/ZnO and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by homogeneous precipitation: steam reforming and oxidative steam reforming. *J. Mol. Catal. A: Chem.*, 268:185-194.
- Sholklapper, T.Z., Radmilovic, V., Jacobson, C.P., Visco, S.J., and Jonghe, L.C.D. (2008). Nanocomposite Ag–LSM solid oxide fuel cell electrodes. *J. Power Sources*, 175:206–210.
- Turco, M., Bagnasco, G., Constantino, U., Marmottini, F., Montanari, T., Ramis, G., and Busca, G. (2004). Production of hydrogen from oxidative steam reforming of methanol i. preparation and characterization of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts from a hydrotalcite-like LDH precursor. *J. Catal.*, 228:43-55.
- Xu, J., Yeung, C.M.Y., Ni, J., Meunier, F., Acerbi, N., Fowles, M., and Tsang, S.C. (2008). Methane steam reforming for hydrogen production using low water-ratios without carbon formation over ceria coated Ni catalysts. *Appl. Catal. A*, 345:119–127.
- Yao, C.Z., Wang, L.C., Liu, Y.M., Wu, G.S., Cao, Y., Dai, W.L., He, H.Y., and Fan, K.N. (2006). Effect of preparation method on the hydrogen production from methanol steam reforming over binary Cu/ZrO<sub>2</sub> catalysts. *Appl. Catal. A*, 297:151–158.
- Zhang, F.Y., Advani, S.G., and Prasad, A.K. (2008). Performance of a metallic gas diffusion layer for PEM fuel cells. *J. Power Sources*, 176:293–298.
- Zhou, L., Guo, Y., Zhang, Q., Yagi, M., Hatakeyama, J., Li, H., Chen, J., Sakurai, M., and Kameyama, H. (2008). A novel catalyst with plate-type anodic alumina supports, Ni/NiAl<sub>2</sub>O<sub>4</sub>/g-Al<sub>2</sub>O<sub>3</sub>/alloy, for steam reforming of methane. *Appl. Catal. A*, 347:200–207.