

## Performance Evaluation of Cu-SiO<sub>2</sub> Aerogel Catalyst in Methanol Steam Reforming

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### Abstract

Effect of copper content, calcination temperature and activation method on the activity and selectivity of copper-silica aerogel catalysts for hydrogen production from methanol steam reforming was investigated. Results showed the copper content had the highest impact and the activation condition had the lowest impact on the catalyst performance. It was found that Cu-SiO<sub>2</sub> aerogel was a promising catalyst for methanol steam reforming. The only parameter which influences the CO selectivity was copper content. Using the best prepared catalyst, no CO formation was detected in the common condition of reaction. In the used range of feed flow rates, methanol conversion was increased 1.5-2.26 times by increasing the copper content from 7.7 to 13.3wt%. Characteristics/performance relationship showed that the samples in which copper species exist as CuO clusters had the best performance to increase the hydrogen production rate and decrease the CO formation. Formation of CuO clusters was increased by increasing the copper loading and calcination temperature. It was found that due to the reducibility behaviour of copper-silica aerogels the activation method of catalysts had almost no effect on the catalytic performance.

**Keywords:** Copper-Silica Aerogel Catalyst, Hydrogen Production, Activity, CO Selectivity, Methanol Steam Reforming

### 1. Introduction

Hydrogen is a carbon free energy carrier, its combustion in a fuel cell is a clean process which produces only water as an exhaust material [1,2]. Due to safety, storage and transport issues using the fuel cell systems for transportation applications require a small and on-board hydrogen supplier. Methanol steam reforming, MSR, has received particular attention to supply the hydrogen

feed of fuel cells. Methanol is easy to produce and safe to handle, has no C-C bonds, low coke formation, high hydrogen to carbon ratio, low reforming temperature and zero emission of SO<sub>x</sub> and NO<sub>x</sub> [1,3,4].

However, the activity and selectivity of conventional Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts are not sufficient to obtain compact and simple reformers which are desired for mobile applications. CO was produced as an undesired by-product in the MSR process which poisons the platinum (Pt) catalyst on

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the anode of fuel cell. Thus, CO elimination from the reformer gas by further purification processes before entering the fuel cell was required, which complicates the overall process. On the other hand, the objective is to produce the highest amount of hydrogen using the least amount of catalyst to reduce the reformer size and enhance the energy efficiency. Thus, enhancing H<sub>2</sub> production and suppressing CO formation by catalytic or reaction engineering solution is an interesting research area [4-8]. Various researchers attempted to develop an efficient catalyst to this reaction. These catalysts include CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Cu/ZrO<sub>2</sub> [9,10], Pd, Ni, Pt and Rh supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZnO, MgO, La<sub>2</sub>O<sub>3</sub>, NdO<sub>3</sub>, MnO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> [11], Pd/ZnO [12,13], Cu/Zr, Cu/Cr and Cu/Zn on Al<sub>2</sub>O<sub>3</sub> [14,15], Cu-Zr-Y and Cu-Zr-La catalysts [16], Cu/ZnO/ZrO<sub>2</sub> [7], Cu/ZnO [17], Cu/ZrO<sub>2</sub>/CeO<sub>2</sub>; Cu/SiO<sub>2</sub>; Cu/Cr<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> [18], CuO/ZnO/CeO<sub>2</sub>/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [3].

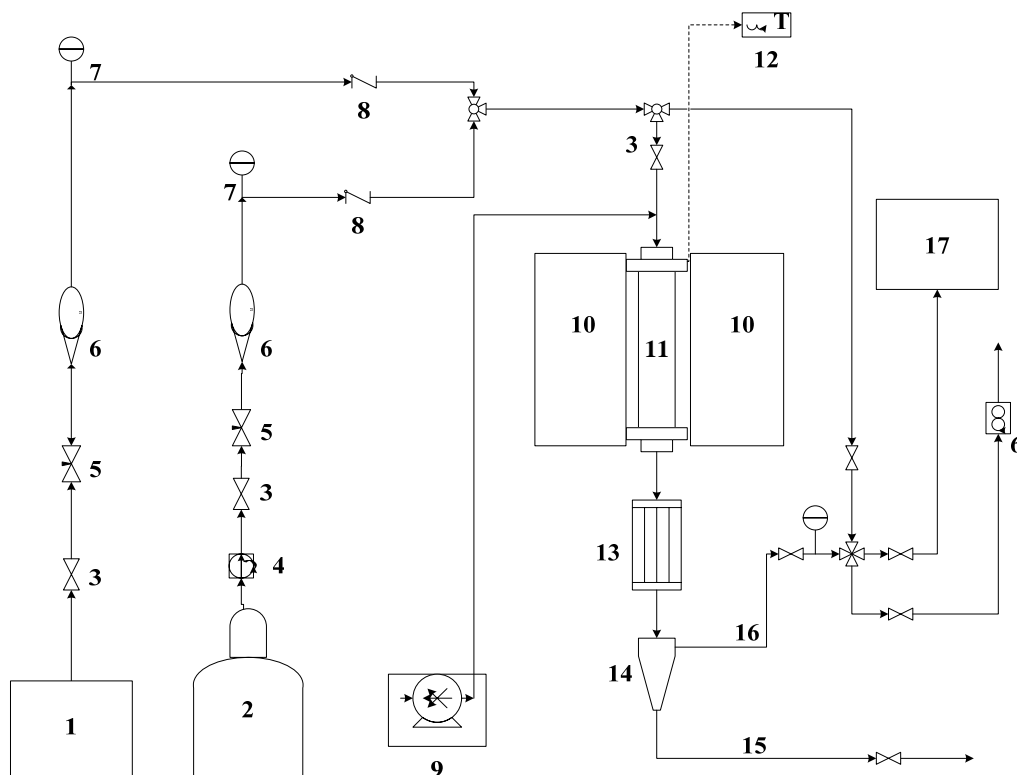
Some unique properties such as large surface area, high porosity and interconnected pores make the aerogels attractive candidates for catalyst application [19,20]. Therefore, in previous work [21] the copper-silica aerogel catalyst was synthesized and characterized in which the aerogel materials were obtained with acceptable properties as catalyst application. In addition to the nature and physical properties of the active and matrix materials, the composition of catalyst and some post-preparation conditions influence the performance of catalyst. Here, the effects of copper content, calcination temperature and activation method on the performance of prepared copper-silica aerogel catalysts in the SRM process were studied to find the

relationship between characteristics-performance and the optimum condition for increasing the hydrogen production rate and decreasing the CO selectivity.

## **2. Experimental**

Detailed catalyst preparation method and characterization were described elsewhere [21]. Copper-silica aerogel was synthesized by cogelation of copper and silica precursors followed by solvent exchange and chemical surface modification and dried at ambient pressure. Then, dried copper-silica aerogels were placed in a furnace and calcined in air with a heating rate of 4°C/min from room temperature to 450 or 700°C, then held at final temperature for 3 h.

The methanol steam reforming reaction was performed at atmospheric pressure in a Pyrex tubular fixed-bed reactor with 4 mm i.d. which was put in a programmable furnace. The liquid feed mixture water: methanol with 2:1 molar ratio was introduced into reactor inlet at desired flow rate (1.2-4.8 ml/h), using a syringe pump (702 SM Titrino, Metrohm) where it was carried by argon stream and vaporized before reaching the catalyst bed. Argon stream flow rate was 30 ml/min. After cooling the reactor effluent, the concentration of reformer gas components including H<sub>2</sub>, CO<sub>2</sub> and CO was measured using an on-line gas chromatography (Agilent Technologies 7890AGC) equipped with HP-Plot/Q (30m, 0.53mm, 40 μm) capillary column and TCD detector. Helium was used as GC carrier gas. A schematic diagram of experimental setup was shown in Fig. 1.



**Figure 1.** Schematic diagram of experimental set-up. 1: Hydrogen generator, 2: Argon cylinder, 3: Valve, 4: Pressure regulator, 5: Needle valve, 6: Flow meter, 7: Pressure indicator, 8: Check valve, 9: Syringe pump, 10: Furnace, 11: Reactor, 12: Temperature controller, 13: Condenser, 14: Gas – liquid separator, 15: Collected liquid, 16: Dry product gas, 17: Gas chromatography.

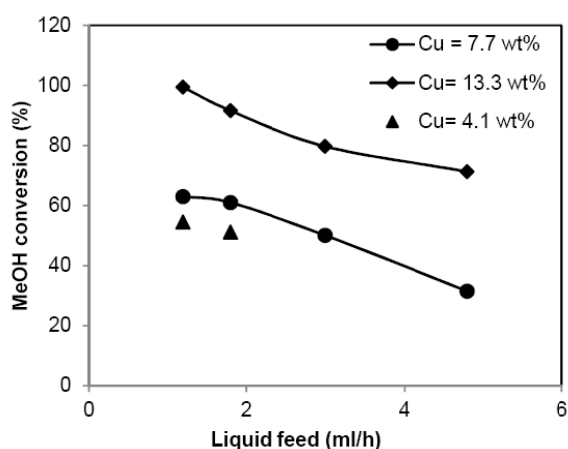
### 3. Results and discussion

#### 3-1. Effect of copper content

Fig. 2 illustrates the activity data of copper-silica aerogel catalysts for three different copper contents. These data were obtained at 300°C. It can be seen that by increasing the copper loading the conversion profiles shift to the higher values, and at a constant feed flow rate the increasing Cu loading increases the activity of catalysts and methanol conversion. For instance, the methanol conversion at 1.2 ml/h of feed flow increased from 63 to 99.4% by increasing the copper content from 7.7 to 13.3% wt. In catalysts with lower copper loading the copper species distributed and entrapped within the silica

matrix as isolated cupric ions. The accessibility of reactant to these entrapped copper species is difficult. Whereas in catalysts with higher Cu contents CuO clusters were also formed on the catalyst [21,22]. Indeed, by increasing the copper loading the appearance of copper as CuO particles in the catalysts was increased. These results showed that CuO clusters were highly active and selective in methanol steam reforming reaction. Also, as seen from FE-SEM images [21] the lower the Cu loading the larger the particle size of the aerogels. Thus, the occlusion possibility of the highly dispersed cupric ions within the larger particles of the matrix increases, while the

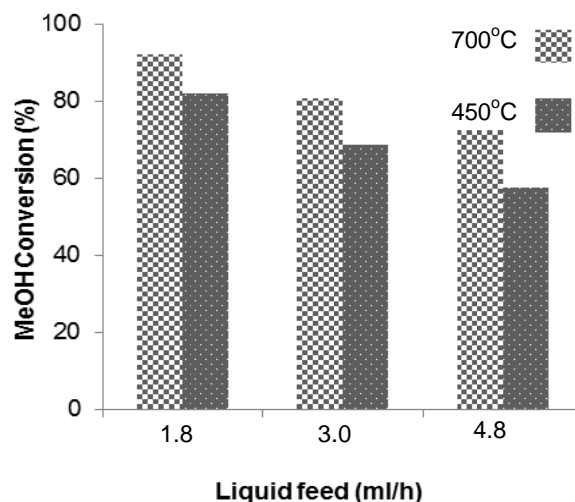
encapsulation of larger CuO clusters within smaller aerogel particles was reduced. Therefore, CuO clusters in the catalysts with higher copper loading were more accessible for the reactants molecules which increases the reaction rate for catalysts with higher copper loading. Here, the copper-silica aerogel with 13.3 wt% of Cu has the highest activity and was selected to carry out the following experiments.



**Figure 2.** Effect of copper content of Cu-SiO<sub>2</sub> aerogel catalysts on methanol conversion versus liquid feed flow.

### 3-2. Effect of calcination temperature

Copper-silica aerogels were calcined at 450 and 700°C. The obtained methanol conversions using these catalysts at different liquid feed flow were shown in Fig. 3. Experiments were done at 300°C using 0.82 g catalyst and S/M=2. As seen, in all feed flows the activity of catalysts which were calcined at 700°C was higher. The differences between the conversions were around 10-15%. From XRD and TPR results reported in previous work [21], XRD patterns of catalyst calcined at 450°C have no diffraction peaks, which with the green color of the catalysts show the highly dispersed isolated copper ions in the matrix.



**Figure 3.** Comparison of catalytic activity of Cu-SiO<sub>2</sub> aerogel catalysts calcined at different temperatures.

While in the patterns of catalysts calcined at 700°C the characteristic peak of CuO was observed. Also, TPR analyses show lower reduction temperature for catalyst calcined at 450°C which is in agreement with the presence of highly dispersed small species, while the catalysts calcined at 700°C had higher reduction temperature related to reduction of larger CuO clusters. Therefore, it is shown that the copper present as isolated copper ions in the catalyst calcined at 450°C while the state of copper in the catalyst calcined at 700°C was predominantly CuO clusters. From the activity results (Fig. 3) it is seen that the CuO cluster is the effective state, indicating higher activity during methanol steam reforming reaction course.

### 3-3. Effect of activation method

All the calcined catalysts were activated prior to use in the reaction. The common activation method of catalysts is the reduction of the catalyst under a steam of H<sub>2</sub> flow at a given temperature. For copper supported catalyst in the methanol steam reforming reaction the activation can be

performed by treatment with the vaporized feed flow, water: methanol 2:1 molar mixture flow, without reduction by H<sub>2</sub> steam [10,23]. Here, the calcined copper-silica aerogel catalysts were activated prior to performance evaluation, both by treatment with the hydrogen stream at three different temperatures, 200, 300 and 400°C for 2 h and by treatment with the feed flow under reaction condition. The activity of catalysts that were activated by the various mentioned methods, by hydrogen at different temperatures or by water/methanol mixture, were investigated and the obtained methanol conversion and hydrogen production as a function of feed flow are shown in Fig. 4. Reaction temperature in these experiments was 300°C. As seen, the activation temperature or mode has almost no influence

on the copper-silica catalyst activity and the catalysts show nearly the same activity and hydrogen production at different feed flow. This is perhaps due to the easy reducibility of copper-silica aerogel catalyst. Copper-silica aerogel catalysts were reduced at relatively low temperature at around 210-270°C as obtained in TPR analysis of catalysts [21]. Therefore, they are easily activated during reaction course regardless of pre-reduced temperature.

Comparison between catalyst activity of selected catalysts as methanol conversion or hydrogen production was given in Table 1. This comparison was performed at similar condition with various catalysts and indicates that the prepared catalyst in this work shows good activity in the methanol steam reforming reaction.

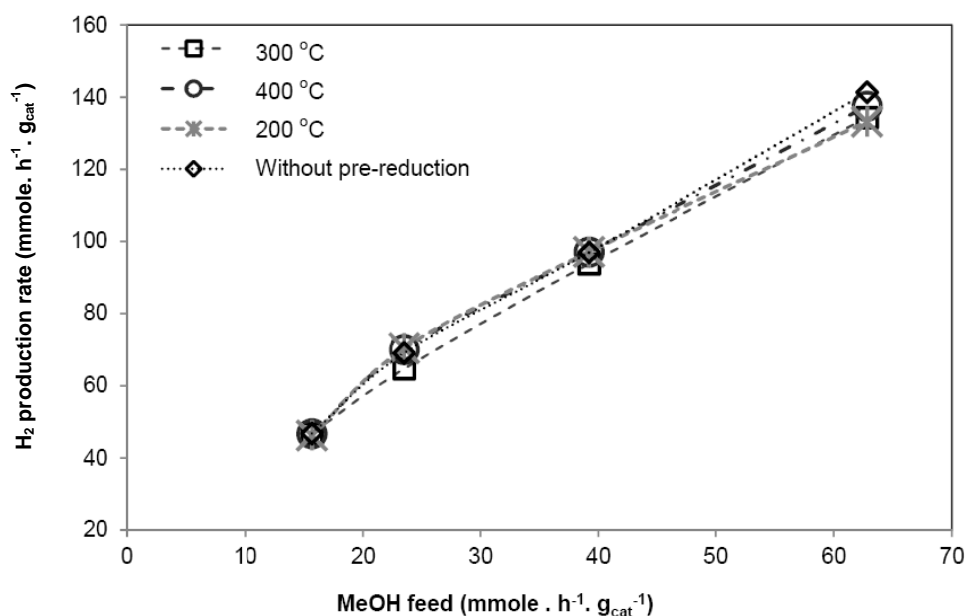


Figure 4. Effect of H<sub>2</sub> pre-reduction temperature on catalytic activity of Cu-SiO<sub>2</sub> aerogel catalysts.

**Table 1.** Comparison between catalyst activity of selected catalysts in the methanol steam reforming reaction.

Catalyst	T <sub>reaction</sub> (°C)	Feed flow or WSHV	MeOH Conversion (%)	H <sub>2</sub> production rate or H <sub>2</sub> Yield (%)
Cu-Zn-Zr-Al [24]	300	24 mmole CH <sub>3</sub> OH. g <sub>cat</sub> <sup>-1</sup> . h <sup>-1</sup>	78	-
Cu-Zn-Zr [24]	300	24 mmole CH <sub>3</sub> OH. g <sub>cat</sub> <sup>-1</sup> . h <sup>-1</sup>	46	-
Cu-Zn-Ce-Al [24]	300	24 mmole CH <sub>3</sub> OH. g <sub>cat</sub> <sup>-1</sup> . h <sup>-1</sup>	51	-
This work	300	23.5 mmole CH <sub>3</sub> OH. g <sub>cat</sub> <sup>-1</sup> . h <sup>-1</sup>	94.7	-
Mo <sub>2</sub> C/ZrO <sub>2</sub> [25]	400	WHSV= 2.67 h <sup>-1</sup>	91	68.5mmole. h <sup>-1</sup> . g <sub>cat</sub> <sup>-1</sup>
This work	300	WHSV= 2.67 h <sup>-1</sup>	82.4	97mmole. h <sup>-1</sup> . g <sub>cat</sub> <sup>-1</sup>
NiSn/MgO/Al <sub>2</sub> O <sub>3</sub> [26]	300	WHSV=4.33 h <sup>-1</sup>	-	22.5 %
	350	WHSV=4.33 h <sup>-1</sup>	-	60 %
This work	300	WHSV=4.25 h <sup>-1</sup>	-	73 %
	350	WHSV=4.25 h <sup>-1</sup>	-	89 %

### 3-4. CO selectivity

Among the studied parameters, the most affecting factor on the CO formation was the copper loading; so that increasing the copper content in the Cu-SiO<sub>2</sub> aerogel catalysts reduced the CO formation significantly. According to activity and selectivity results, we focused on the copper-silica aerogel with 13.3wt% Cu content. The Cu-SiO<sub>2</sub> aerogel catalyst with 13.3% of copper has very low CO selectivity so that in the common condition of MSR no CO formation was detected. For CuO/CeO<sub>2</sub> catalyst with various copper contents the CO selectivity was obtained about 3-6% at 300°C using 20 ml CH<sub>3</sub>OH.g<sub>cat</sub><sup>-1</sup>.min<sup>-1</sup>[2], while in this work in the range of 7.6-30.5 ml CH<sub>3</sub>OH.g<sub>cat</sub><sup>-1</sup>.min<sup>-1</sup> at 300°C no CO formation was detected. For various catalysts such as Cu-Zn-Zr-Al, Cu-Zn-Zr and Cu-Zn-Ce-Al the CO selectivity was reported as 3-12 % at 300°C and contact time of 0.15 kg catalyst.s/mmol CH<sub>3</sub>OH or 24 mmol CH<sub>3</sub>OH.h<sup>-1</sup>.g<sub>cat</sub><sup>-1</sup>[24]. At this temperature and contact time using the prepared CuO/SiO<sub>2</sub> catalyst with 13.3% copper no CO formation was observed. Using Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst at

methanol conversions above 70% CO were present [27], while in this work methanol convert above 90% without any CO presence. For Pd/ZnO catalyst even at 250°C CO selectivity was between 4-20% using the water to methanol molar ratio of 1.1 at methanol feed flow rate of 32-100 mmole.h<sup>-1</sup>.g<sub>cat</sub><sup>-1</sup>[28]. These observations demonstrate that Cu-SiO<sub>2</sub> aerogel was a promising catalyst for MSR process. In general, the catalyst mass, calcination and activation temperature had no significant effect on the CO selectivity, and the CO formation was detected at temperatures higher than 325°C for cases in which the complete conversions were almost achieved. This result showed that CO formed as a secondary product through the reverse water gas shift reaction and can be avoided by using the feed rates in which the complete conversion was achieved at lower temperature or by using the higher temperatures far from the complete conversion. According to these observations, copper-silica aerogel catalysts had very high selectivity to production of H<sub>2</sub> and CO<sub>2</sub> from MSR reaction.

#### 4. Conclusions

Hydrogen production from MSR reaction using Cu-SiO<sub>2</sub> aerogel catalyst was investigated. Copper content in the final catalyst had significant effect on the performance so that by increasing the copper loading in the aerogel catalysts the hydrogen production rate increased and the formation of CO decreased. Also, the catalysts calcined at higher temperature show better activity. Catalyst activation can be performed during reaction course without the pre-reduction by hydrogen flow. With the exception of copper content the other parameters had no remarkable influence on the CO selectivity and CO was formed as consecutive product almost at complete methanol conversions at temperatures higher than 325°C, which showed the used catalysts have very high desired selectivity. The results showed that in the studied condition, Cu-SiO<sub>2</sub> aerogel catalyst with 13.3 wt% of copper which was calcined at 700°C was a catalyst with good activity and much desired selectivity for MSR reaction to maximize the H<sub>2</sub> production and minimize the CO formation.

#### References

- [1] Chang, C.C., Chang, C.T., Chiang, S.J., Liaw, B.J., and Chen, Y.Z., "Oxidative steam reforming of methanol over CuO/ZnO/CeO<sub>2</sub>/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts", *Int. J. Hydrogen Energ.*, 35, 7675 (2010).
- [2] Udani, P.P.C., Gunawardana, P.V.D.S., Lee, H.C., and Kim, D.H., "Steam reforming and oxidative steam reforming of methanol over CuO-CeO<sub>2</sub> catalysts", *Int. J. Hydrogen Energ.*, 34, 7648 (2009).
- [3] Huang, G., Liaw, B.J., Jhang, C.J., and Chen, Y.Z., "Steam reforming of methanol over CuO/ZnO/CeO<sub>2</sub>/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts", *Appl. Catal. A*, 358, 7 (2009).
- [4] Perez-Hernandez, R., Gutierrez-Martinez, A., Palacios, J., Vega-Hernandez, M., and Rodriguez-Lugo, V., "Hydrogen production by oxidative steam reforming of methanol over Ni/CeO<sub>2</sub>eZrO<sub>2</sub> catalysts", *Int. J. Hydrogen Energ.*, 36, 6601 (2011).
- [5] Turco, M., Cammarano, C., Bagnasco, G., Moretti, E., Storaro, L., Talon, A., and Lenarda, M., "Oxidative methanol steam reforming on a highly dispersed CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by a single-step method", *Appl. Catal. B*, 91, 101 (2009).
- [6] Agrell, J., Birgersson, H., Boutonnet, M., Melian-Cabrera, I., Navarro, R. M., and Fierro J. L. G., "Production of hydrogen from methanol over Cu/ZnO catalysts promoted by ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>", *J. Catal.*, 219, 389 (2003).
- [7] Matsumura, Y. and Ishibe, H., "High temperature steam reforming of methanol over Cu/ZnO/ZrO<sub>2</sub> catalysts", *Appl. Catal. B*, 91, 524 (2009).
- [8] Agrell, J., Birgersson, H., and Boutonnet, M., "Steam reforming of methanol over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst: a kinetic analysis and strategies for suppression of CO formation", *J. Power Sources*, 106, 249 (2002).
- [9] Szizybalski, A., Girgsdies, F., Rabis, A., Wang, Y., Niederberger, M., and Ressler, T., "In situ investigations of structure-activity relationships of a Cu/ZrO<sub>2</sub> catalyst for the steam reforming of methanol", *J. Catal.*, 233, 297 (2005).
- [10] Purnamaa, H., Girgsdies, F., Ressler, T., Schattka, J.H., Caruso, R.A., Schomacker, R., and Schlogl, R., Activity and selectivity of a nanostructured CuO/ZrO<sub>2</sub> catalyst in the steam reforming of methanol", *Catal. Lett.*, 94, 61 (2004).
- [11] Takezawa, N., and Iwasa, N., "Steam reforming and dehydrogenation of methanol: Difference in the catalytic functions of copper and group VIII metals", *Catal. Today*, 36, 45 (1997).

- [12] Chin, Y.H., Dagle, R., Hu, J., Dohnalkova, A.C., and Wang, Y., "Steam reforming of methanol over highly active Pd/ZnO catalyst", *Catal. Today*, 77, 79 (2002).
- [13] Conant, T., Karim, A.M., Lebarbier, V., Wang, Y., Girgsdies, F., Schlogl, R., and Datye, A., "Stability of bimetallic Pd-Zn catalysts for the steam reforming of methanol", *J. Catal.*, 257, 64 (2008).
- [14] Lindström, B., Pettersson, L.J., and Menon, P.G., "Activity and characterization of Cu/Zn, Cu/Cr and Cu/Zr on alumina for methanol reforming for fuel cell vehicles", *Appl. Catal. A*, 234, 111 (2002).
- [15] Breen, J.P. and Ross, J.R.S., "Methanol reforming for fuel-cell applications: development of zirconia-containing Cu-Zn-Al catalysts", *Catal. Today*, 51, 521 (1999).
- [16] Clancy, P., Breen, J.P., and Ross, J.R.H., "The preparation and properties of coprecipitated Cu-Zr-Y and Cu-Zr-La catalysts used for the steam reforming of methanol", *Catal. Today*, 127, 291 (2007).
- [17] Danwittayakul, S., and Dutta, J., "Zinc oxide nanorods based catalysts for hydrogen production by steam reforming of methanol", *Int. J. Hydrogen Energ.*, 37, 5518 (2012).
- [18] Frank, B., Jentoft, F.C., Soerijanto, H., Krohnert, J., Schlogl, R., and Schomacker, R., "Steam reforming of methanol over copper-containing catalysts: Influence of support material on microkinetics", *J. Catal.*, 246, 177 (2007).
- [19] Dunn, B.C., Cole, P., Covington, D., Webster, M.C., Pugmire, R.J., Ernst, R.D., Eyring, E.M., Shah, N., and Huffman, G.P., "Silica aerogel supported catalysts for Fischer-Tropsch synthesis", *Appl. Catal. A*, 278, 233 (2005).
- [20] Dominguez, M., Taboada, E., Molins, E., and Llorca, J., "Co-SiO<sub>2</sub> aerogel-coated catalytic walls for the generation of hydrogen", *Catal. Today*, 138, 193 (2008).
- [21] YousefiAmiri, T. and Moghaddas, J., "Cokeless copper-silica aerogel as a catalyst in hydrogen production from methanol steam reforming", *Int. J. Hydrogen Energ.*, 40, 1472 (2015).
- [22] Takezawa, N., Kobayashi, H., Hirose, A., Shimokawabe, M., and Takahashi, K., "Steam reforming of methanol on copper-silica catalysts; effect of copper loading and calcination temperature on the reaction", *Appl. Catal.* 4, 127 (1982).
- [23] Idem, R.O., Production of hydrogen from the low-temperature steam reforming of methanol. Ph.D. thesis, University of Saskatchewan, Saskatchewan., (1995).
- [24] Jones, S.D. and Hagelin-Weaver, H.E., "Steam reforming of methanol over CeO<sub>2</sub>- and ZrO<sub>2</sub>-promoted Cu-ZnO catalysts supported on nanoparticle Al<sub>2</sub>O<sub>3</sub>", *Appl. Catal. B*, 90, 195 (2009).
- [25] Lin, S.S.Y., Thomson, W.J., Hagensen, T.J., and Ha, S.Y., "Steam reforming of methanol using supported Mo<sub>2</sub>C catalysts", *Appl. Catal. A*, 318, 1121 (2007).
- [26] Penkova, A., Bobadilla, L., Ivanova, S., Dominguez, M.I., Romero-Sarria, F., Roger, A.C., Centeno, M.A., and Odriozola, J.A., "Hydrogen production by methanol steam reforming on NiSn/MgO-Al<sub>2</sub>O<sub>3</sub> catalysts: The role of MgO addition", *Appl. Catal. A*, 392, 184 (2011).
- [27] Du, X., Shen, Y., Yang, L., Shi, Y., and Yang, Y., "Experiments on hydrogen production from methanol steam reforming in the microchannel reactor", *Int. J. Hydrogen Energ.*, 37, 12271 (2012).
- [28] Karim, A., Conant, T., and Datye, A., "The role of PdZn alloy formation and particle size on the selectivity for steam reforming of methanol", *J. Catal.*, 243, 420 (2006).