

Design of Steam Reforming Reactor for Converting Methanol into Hydrogen Using an Ultrasonic Nebulizer as Liquid Feeder and Polymer Liquid Processed CuO/ZnO/Al₂O₃ Particles as Catalyst

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Abstract: A catalyst of CuO/ZnO/Al₂O₃ has been synthesized using the simple heating of a nitrates precursor in a polymer solution. A steam reforming reactor for converting methanol into hydrogen using an ultrasonic nebulizer as a liquid feeder and the prepared catalyst was also be designed. The produced catalyst particles had relatively small sizes (ranging from about 70 – 120 nm) and were softly agglomerated. Testing of the conversion reacting performance showed the presence of the starting temperature for methanol to hydrogen conversion to be 300°C, above which the conversion occurred and below which the conversion disappeared. These two works (synthesis of catalyst and design of reactor) are promising developments of direct methanol fuels cells to be used in automobiles technology.

Keywords: steam reforming methanol reactor, direct methanol fuel cell, catalyst.

1. Introduction

Direct methanol fuel cells (DMFCs), which are predicted to be the power source for future automobile technology, provide many advantages over the well-known conventional combustion engines [1]. Fuel cells are environmentally green, produce nearly zero gas and sound pollutant emissions, and exhibit high efficiency. Due to thermodynamic limitations, the efficiency of a typical combustion engine is usually less than 30%, but a fuel cell can reach above 80%.

Recent unfortunate impacts caused by reductions in fossil energy stocks have greatly motivated intensive research to various renewable energy resources, including the fuel cell. However, a critical problem that must be solved to further develop the fuel cell for automobile technology is how to supply enough hydrogen gas constantly into the cell to produce electricity. Fuel cells work by absorbing oxygen and hydrogen gases to generate chemical reactions, and the products of the reactions are water and electricity. Oxygen can be absorbed directly from the atmosphere due to its abundance in the atmosphere. However, because hydrogen is less abundant content in the atmosphere, a mechanism for supplying hydrogen must be developed.

One common approach for supplying hydrogen into fuel cells is by storing hydrogen in high pressure tanks, from which the hydrogen is supplied little by little to the cell. The volume and pressure of the hydrogen tanks determine the distance that can be traveled by the automobile. However, this approach is risky because hydrogen is a very explosive gas. Unexpected collisions of vehicles can initiate a big explosion and might cause great damage to the surroundings. The trouble with hydrogen is that it is hard to store and also highly volatile [2]. These reasons greatly motivated the search for safer approaches to make fuel cell driven automobiles widely accepted by consumers.

One promising approach for developing a safe fuel cell driven automobiles is by using DMFCs, instead of fuel cells in their basic architecture. In a DMFC, the storage tanks in the automobile are not filled with hydrogen but with safer materials which are easily convertible into hydrogen. Since hydrogen storage is not required, the risk of explosion can be avoided. One potential

convertible material is methanol. With the help of a specific catalyst, methanol can be converted into hydrogen at temperatures below 500°C. Methanol also offers a high conversion rate and produces less by-products, other hydrocarbon fuels [2].

The implication of this approach is that additional equipment must be developed, namely a steam reforming methanol reactor (SRMR). A mixture of water and methanol are brought into the reformer and one of the products is hydrogen gas that will be used to fuel the cell. The best type of catalyst for SRMR, the method of synthesizing the catalyst, as well as the design of the SRMR, do not appear to have been optimized. These situations prompted us to investigate an alternative method synthesizing of the catalyst and an alternative design for the SRMR.

The present work has two objectives. First is to investigate the method of synthesizing CuO/ZnO/Al₂O₃ catalyst with particle sizes in nanometers or nearly nanometers. Indeed, many types of catalysts such as Cu/ZnO [2], Pd/ZnO [3], and Ni/Al₂O₃ and Ru/Al₂O₃ [4] have been explored by many authors for this purpose. The CuO/ZnO/Al₂O₃ catalyst was selected because it is simple in synthesis. We used a method of simple heating of a precursor in a polymer liquid environment because simplicity and it has been successfully used by us to produce many kinds of oxide particles [5-10]. This method can also produce the particles for less than one hour and the size of particles can reach the nanometer order. The second objective is the design of SRMR and to investigate the conversion of methanol into hydrogen by using the prepared catalyst. The initial process of conversion is feeding a methanol and water mixture into an evaporator to generate a vapor and bring the vapor into a catalyst container to generate the conversion reaction. Many researchers used syringe pumps to feed the mixture of methanol and water into the evaporator. We are doubtful this approach might create unexpected problems. In order to generate a complete conversion reaction, the molar ratio of water and methanol must be kept to at 1:1 as mandated by the following reaction, $\text{CH}_3\text{OH} + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}_2$. If we use a syringe pump, we are doubtful to face the following problems. Since the syringe tube contains still water and methanol, the mixture might deviate from homogeneity, resulting in the deviation of the molar ratio of water and methanol leaving the syringe needle from 1:1. Another potential problem is the size of the

droplets leaving the syringe needle might be large so it would need relatively high temperatures or long resident times of heating to evaporate the droplets completely.

In the present work, however, we used an ultrasonic nebulizer to feed the methanol and water mixture into the evaporator. This approach might provide several advantages. First, the mixture of water and methanol in the nebulizer might be kept homogeneous due to the constant shaking of the mixture by ultrasonic waves. Second, the droplet sizes produced by the nebulizer are very small, typically less than 20 μm , so that in the evaporation process, we need only low temperatures and a short resident time. Third, the rate of feeding the mixture of methanol and water droplets can be controlled precisely using a flow meter attached to the outlet of the carrier gas tube.

2. Materials and Methods

2.1 Catalyst Preparation

Precursors used for the preparation of the catalyst were $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Kanto Chemicals, Japan), $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Kanto Chemicals, Japan), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Kanto Chemicals, Japan), and polyethylene glycol (PEG) (Wako Pure Chemicals, Japan, average molecular weight of 20,000). Based on previous studies, the molar ratio of the metallic elements in the precursor were fixed at $\text{Cu}/\text{Zn}/\text{Al} = 2/1/0.1$ [11,12]. All metallic nitrates were completely dissolved in distilled water followed by adding an appropriate amount of PEG. The mixture was then heated up to about 100°C while stirring until the PEG completely dissolved and resulted in a clear viscous liquid. The liquid was then put in an alumina crucible, followed by heating to a required temperature in an atmospheric environment. Initially, the temperature was raised linearly up to the required temperature for 30 minutes, followed by natural cooling back to room temperature. Several samples were synthesized at different heating temperatures to inspect the effects on temperature on the particle properties.

2.2 Design of Reactor

The main components on the reactor are an ultrasonic nebulizer, a carrier gas, a liquid evaporator, a temperature controllable catalyst container, a condenser, and a gas outlet. The schematic of the reactor is shown in Fig. 1

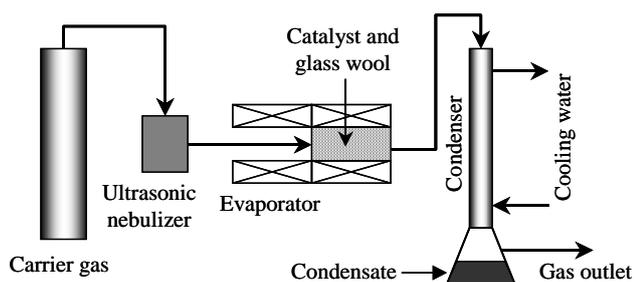


Figure 1. Schematic of reactor design.

The ultrasonic nebulizer is used to generate droplets from the water and methanol mixture. The droplet size depends on the surface tension of the liquid, fluid density, and ultrasonic frequency [12]. For a typical ultrasonic nebulizer, the droplet diameter varies from micrometer to tens of micrometers.

The liquid evaporator was made of a glass tube wound by a heating element, and fixed at a temperature of about 150°C . This temperature is relatively far above the evaporation temperature of water and methanol. Droplets were carried from the nebulizer to the evaporator using a nitrogen gas.

Water and methanol vapor from the evaporator moves to the catalyst container, which was made out of a stainless steel tube. The tube was 10 cm in length and 5 cm in inner

diameter. A catalyst of $\text{ZnO}/\text{CuO}/\text{Al}_2\text{O}_3$ powder was mixed with a large fraction of glass wool and then put inside the tube. The reason for using the glass wool is to allow the vapor and the produced gases to flow easily inside the container. The container tube was wound with a heating element, the temperature of which can be controlled by a temperature controller. The temperature of the container can be set in a range from 100°C up to 600°C .

A condenser was used to collect the unreacted water and methanol mixture. We used a tandem condenser consisting of two condensers with a total length of about 1.1 meters and was cooled using water mixed with ice blocks.

2.3 Reactor Operation

Testing of the reformer was performed by initially flowing nitrogen gas through the reactor for 30 minutes with a rate of 1 l/min to remove air from the reactor and leave only nitrogen gas in the reactor. Hydrogen gas was then flowed through the catalyst to convert the CuO on the surface into Cu as an active element according to the reaction $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$. Details of the reduction are given as follows. Initially, the outlet of the catalyst container was closed. Hydrogen gas was flowed into the catalyst container, and a few minutes later the inlet of the container was closed. The hydrogen gas was trapped in the catalyst container for ten minutes to give enough time for the reduction of $\text{CuO} \rightarrow \text{Cu}$ on the catalyst's surface. Finally, the outlet and the inlet of the catalyst container were opened to allow the trapped gases to flow out. The reduction steps were repeated three times to ensure that as many as possible of the CuO has converted into Cu.

The nebulizer was then turned-on and few minutes later (to ensure that equilibrium production of droplet was arrived) nitrogen gas was flowed at a flow rate of 0.2 l/min for one hour. The temperature of the catalyst container was set at the designated temperature. The experiment was repeated at different catalyst temperatures (different reaction temperatures).

2.4 Characterizations

Catalysts synthesized using a polymer liquid method were characterized using a field emission scanning electron microscope (FE-SEM Hitachi S5000) and an X-ray diffractometer (Rigaku RINT2000). Elemental analysis was done using the EDX method (JEOL JSM-6360 LA). The characteristic of methanol conversion was determined indirectly by comparing the volume of methanol and water mixture left by the nebulizer with the volume of the mixture collected by the condenser. In the present study, we were unable to count the fraction of each gas flowing out the reactor because of the unavailability of gas chromatography equipment.

3. Results and Discussion

SEM images of samples prepared at different heating temperatures of 450°C , 500°C , and 600°C , are shown in Fig. 2. The heating temperatures were set above the decomposition temperature of PEG (about 400°C) to ensure that after heating the PEG has decomposed completely and left only particles. We selected the heating temperatures to be slightly above the decomposition temperature of the PEG to produce catalyst particles having small sizes. Previous studies showed that the sizes of the particles increase with heating temperature [8-10]. For catalyst applications, we need particle sizes as small as possible to increase the reaction rate caused by the high surface area. At the three different temperatures used in this work, no significant difference in particle size was observed. The sizes of the particles in all samples varied between 70–120 nm. The possible reason for these results is that the temperature range was narrow, i.e., 150°C .

The XRD patterns of the three samples are shown in Fig. 3. The presence of CuO, ZnO, and Al₂O₃ peaks can be specified in the three diffractograms, although the intensities were different for different samples. The presence of CuO, ZnO, and Al₂O₃ were consistent with reference data PDF 801916, PDF 750788, and PDF 832080, respectively. This result proved that the polymer solution method was able to produce

CuO/ZnO/Al₂O₃ with sizes approaching nanometers. This method provides another advantages such as a short preparation time (less than one hour), which is very short compared to other methods, such as precipitation which needs about one day for forming the particles, softly agglomerated [6] and ready to be scaled-up by just developing large sized-furnace/heating chamber.

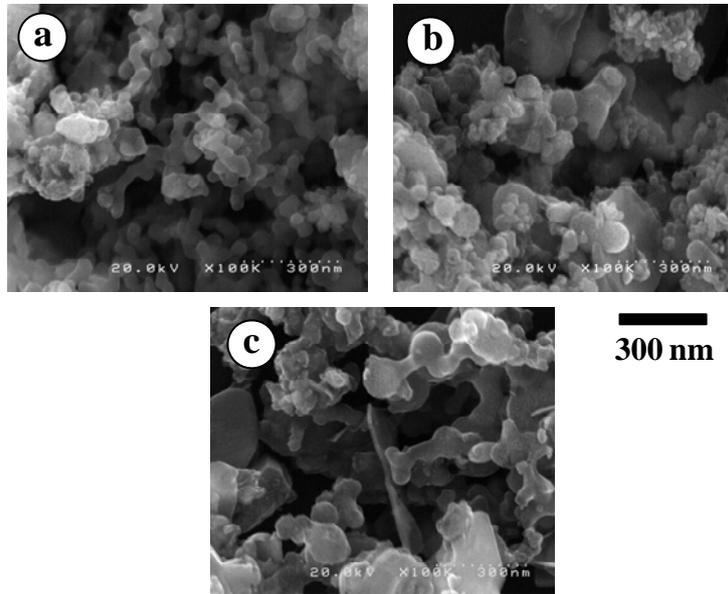


Figure 2. SEM images of samples prepared at different temperatures: (a) 450°C, (b) 500°C, and (c) 600°C.

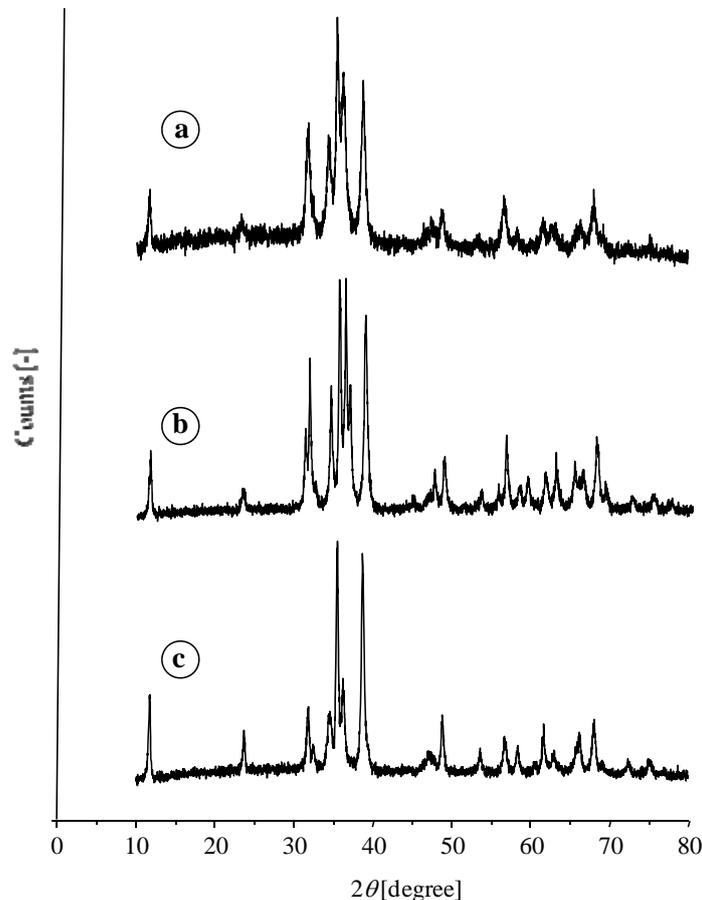


Figure 3. XRD patterns of samples prepared at different temperatures: (a) 450°C, (b) 500°C, and (c) 600°C.

As previously mentioned, the characteristics of conversion were determined indirectly by comparing the volume of the water and methanol mixture leaving the nebulizer and the volume of the mixture collected by the condenser. The catalyst container was set at different temperatures to inspect the effects of the reaction temperature on the conversion efficiency. The measurements were performed at temperatures from 500°C down to 200°C. For each designated temperature, the measurement was repeated three times.

The efficiencies were calculated based on the volume of mixture remaining in the nebulizer and the volume of the mixture collected by the condenser. For calculating the efficiency, the data were corrected with the measurement data when the catalyst was absent. The results of the correction were the volumes of water and methanol vapor reaching the catalyst and the unreacted water and methanol mixture collected by the condenser. The efficiency was calculated by a simple formula, $eff = (V_{reach} - V_{cond.})/V_{reach}$, where V_{reach} is the volume of methanol and water that reached the catalyst and $V_{cond.}$ is the volume of the mixture collected by the condenser. Figure 4 shows the relative conversion efficiencies at different reaction temperatures. As the method was not too accurate, the calculated efficiencies might contain some deviations. Indeed, the fraction of each gas is better determined using gas chromatography equipment, which unavailable for the experiment. In the next study, intensive investigation will be performed, including the use of gas chromatography to analyze precisely the fraction of each gas product. However, the starting temperature for the conversion reaction at around 300°C is acceptable. Our results strongly indicated that the conversion reaction occurs only when the catalyst temperature is above 300°C.

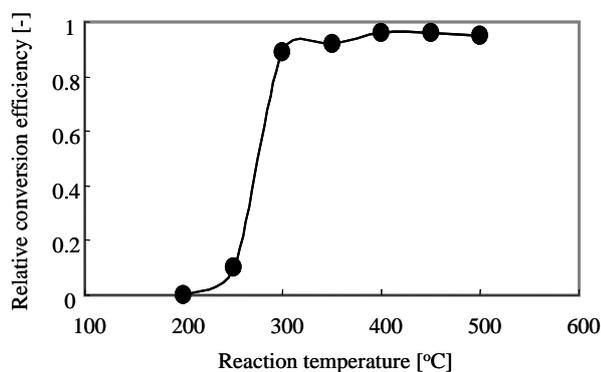


Figure 4. Relative conversion efficiencies at different heating temperatures for sample prepared at 600°C.

To make sure that the gas produced by the catalytic reaction contained hydrogen, we ignited the gas leaving the condenser with a match. We did not see any burning color after ignition, but when we brought a piece of paper to the outlet, the paper ignited immediately. This meant that after ignition, the outgoing gas had burned but was not visible to the naked eyes. This is typical of hydrogen burning [13]. This simple observation was repeated at different reaction temperatures. We observed consistent results with the amount of the mixture collected by the condenser. The same burning phenomenon was observed at other temperatures above 300°C, but when the reaction temperatures were below 300°C, the paper did not burn, indicating that the hydrogen content in the outgoing gas was zero or nearly zero.

Based on the above observations, we identified a polymer process production of the CuO/ZnO/Al₂O₃ catalyst that is very promising for producing catalysts having small sizes, very quick in process, and readily scaled-up. Further investigation is

required on how to greatly reduce the particle sizes, i.e., several nanometers or tens of nanometers to enhance the specific surface area. The steam reforming reactor using an ultrasonic nebulizer to feed the liquid mixture in the form of droplets into an evaporator and a catalyst container is also promising for developing DMFCs system for automobile applications. Further investigation is required on how to design more compact equipment.

4. Conclusion

Catalysts from the CuO/ZnO/Al₂O₃ particles have been synthesized by a simple heating of metallic nitrate precursors in a liquid of PEG at temperatures above the decomposition temperature of the PEG. The PEG was used to minimize the tendency of particles to agglomerate during the synthesis process. A reactor for converting methanol into hydrogen has also been developed with a key component being the use of ultrasonic nebulizer as a liquid feeder, instead of a syringe pump as reported by many authors. Using the prepared catalyst, we observed a sharp change in the conversion behavior at 300°C, above which the conversion occurred and below which the conversion did not occur. This method has potential for designing a direct methanol fuel cell for automobile technology.

Acknowledgements

This work was supported by a grant from *Riset KK ITB 2008*, Bandung Institute of Technology.

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