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H_2 Production by Methanol Steam Reforming over Anodized Aluminum Oxide

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Abstract
In this work, preparation conditions of AAO with regular pores and uniform thickness has been optimized. The two types of AAO, AAO as synthesized and hydrated AAO (by HWT) were prepared and impregnated with Cu and Zn. The surface morphology and Cu content were analyzed by FE-SEM and EDAX measurements.
The difference in BET surface area and its effect on Cu impregnation has also been discussed. The activity of the catalysts for methanol conversion was tested and the Cu-AAO catalysts prepared by dipping method several times showed promising result (73%) with 100% selectivity towards H_2*. Addition of Zn further increased the conversion to 97%.*

Keywords: *Anodized Aluminum Oxide, Methanol Reforming,* H_2 *Production*

I. INTRODUCTION

Currently, much attention is focused on fuel cells as a clean and efficient source of electricity for both mobile and stationary applications [1,2]. Fuel cells need hydrogen or hydrogen rich feed gas as fuel. Several proven technologies such as steam reforming, auto-thermal reforming, partial oxidation and water gas shift can be used to extract hydrogen from fuels like gasoline, diesel, LPG, methane, ethanol and methanol [3–5]. Especially, methanol is a promising candidate to produce hydrogen as it doesn't have inter carbon (C-C) bonds that require high energy to breakup, hence relatively low reforming temperature (200~300°C). Hydrogen, when stored in liquid form at –253°C consists of 33.6 mol H_2/liter whereas methanol (which can be stored at room temperature) gives 49.4 mol (by partial oxidation) ~74 mol (by steam reforming) H_2/liter which makes methanol an attractive source of H_2 and easily transportable fuel [3].

Present technology for methanol reforming uses packed-bed catalytic reactors that suffer from a number of inherent problems such as very steep temperature gradients caused by the poor thermal conductivity of the catalyst bed as well as the large pressure loss through the bed. The temperature gradient in the reactor can cause a hot spot which results in poor performance due to deactivation by catalyst sintering and generation of a large amount of CO [3,6,7]. To overcome this, a metal honeycomb type reactor has been suggested as a promising solution as these reactors allow rapid heat transfer along the axial direction of the reactor by conduction through the wall, thereby reducing the temperature gradient. The reactor is usually made of a high conductivity metal such as aluminum [3] and has a large metal area on which a catalyst layer can be coated or grown. This type of reactor is characterized by a low pressure drop and easy to scale up or scale down.

In the case of catalyst coating, the bonding between the metal surface and the catalyst layer must be strong enough to prevent peeling of the layer. Simple catalyst slurry coating on the metal surface often does not result in strongly adhered catalyst layer on the metal surface [8]. In contrast, a strongly bonded aluminum oxide layer can be first grown by the method of anodic oxidation of the aluminum metal, and the layer may serve as a catalyst support by doping the catalytically active metals, mainly Cu. Nanoporous anodic aluminum oxide (AAO) has received considerable attention because of the self-organization of vertical pores to form a hexagonal array with a controlled and narrow distribution of pore diameters and inter pore distances [9,10].

In this study, anodic aluminum oxide (AAO) supported catalysts are developed. This sort of catalysts has been applied in various fields such as methane steam reforming [11], VOC combustion [12,13] and ammonia decomposition [14]. First an AAO layer was grown on the surface of the aluminum and then the active metal components are deposited into the pores of the AAO layer by a simple dipping method, in which the time of dipping is varied, or by a successive dipping method, in which the dipping time is fixed and dipping, drying and calcination steps are repeated. Thus prepared catalysts are tested for the methanol steam reforming.

II. EXPERIMENTAL

Catalyst Preparation

Aluminum sheets (5X5 cm) were first washed with acetone for 3 min in an ultrasonic bath, degreased in aqueous solution of 1M NaOH for 3 min at room temperature and then immersed in a 6 vol. % HNO_3 solution for 1 min at room temperature. The aluminum sheets were washed with deionized water and dried. Thus pretreated aluminum sheets were anodized on both sides of the sheet in 0.3 M oxalic acid solution for 6 h at 40V at 25°C [9,10]. After the anodization, the aluminum sheets are dried at 80°C for 6 h and calcined at 350°C for 3 h in order to eliminate the residual oxalic acid. These are named as AAO. The catalyst coating on both sides of this AAO support is carried out in two methods.

Simple Dipping

I. AAO is directly impregnated with 0.25 M copper nitrate solution for different times (3 h, 9 h and 12 h) and are dried (Cu-AAO-3 h, Cu-AAO-9 h and Cu-AAO-12 h).

II. AAO is subjected to hot water treatment (HWT) by boiling AAO in water at 90°C for 1 h, dried in oven at 150°C (AAO-HWT). The AAO-HWT is impregnated with 0.25 M copper nitrate solution for 30, 60 and 90 min and dried in oven (Cu-AAO-HWT-30 min, Cu-AAO-HWT-60 min and Cu-AAO-HWT-90 min).

SUCCESSIVE DIPPING

III. AAO is dipped in 0.25 M copper nitrate solution for 1 h and then dried and calcined. This is repeated for five times and labeled as Cu-AAO-1, Cu-AAO-2, Cu-AAO-3, Cu-AAO-4 and Cu-AAO-5.

IV. The catalyst preparation method above is repeated using mixed solution of copper nitrate and zinc nitrate solution of each 0.25 M and represented as Cu-Zn-AAO-1, Cu-Zn-AAO-2, Cu-Zn-AAO-3, Cu-Zn-AAO-4 and Cu-Zn-AAO-5.

After dipping, the catalyst was dried at 80°C for 6 h and calcined at 350°C for 4 h. Before reaction the catalyst was reduced at 300°C for 150 min under a flow of 10% H_2 and balance He at 50 ml/min.

Characterization

The surface morphology of AAO was measured on a FE-SEM (JSM 6701F) machine at an accelerating voltage of 10 KV. The copper content in the catalyst samples was analyzed by EDAX (Hitachi, Model: EDX-350) attached to FE-SEM (Hitachi, Model: S-4300). Prior to the analysis the sample surface is coated with Pt to enhance the conductivity of the sample. The surface area was measured on a Quanta chrome machine (Model: Quadrasorb SI) by N_2-adsorption at 77 K and the surface area is analyzed by BET equation. XRD profiles were measured on a Rigaku Powder Diffractometer (D/Max-2500) using Cu-Kα radiation in the 2θ range of 10–80.

Catalytic Activity Experiment

Steam reforming of methanol is carried out in a fixed bed reactor over a temperature range of 100–300°C at atmospheric pressure. The catalyst was cut into pieces (2~3 mm^2 size) and packed into a 1/4 inch quartz tube reactor. The temperature of the reactor was increased at a rate of 1°C/min. A methanol and a water saturator were used separately to vaporize the liquid feed. He was used as a carrier gas to carry the vapors from each saturator and flow rate of He was controlled by using mass flow controllers. A water circulating bath is used to control each the temperature of each saturator. The feed composition to the reactor was 10% CH_3OH, 15% H_2O and balance He with a total flow rate of 100 ml/min. The effluent composition was analyzed online by a gas chromatograph equipped with a thermal conductivity detector (TCD), Porapak Q column was used to separate CO2, CH_3OH and H_2O in the reactor exit gas. The performance of the catalyst was analyzed in terms of methanol conversion. The methanol conversion was defined as the mole ratio of gaseous carbon compounds (CO, CO_2 and DME) in the product stream to the feed methanol.

III. RESULTS AND DISCUSSION

Catalytic Activity

The Cu-AAO series catalysts has lower copper content and exhibited lower conversion compared to the Cu-AAO-HWT catalysts. The Cu-AAO-HWT catalysts showed a conversion of methanol of 12, 15 and 40% at 300°C for Cu-AAO-HWT-30 m, Cu-AAO-HWT-60 m and Cu-AAO-HWT-90 m, respectively (Figure 1) whereas the Cu-AAO catalyst showed a reverse trend, decreasing conversion with increasing dipping time and showed 17% for Cu-AAO-3 h, 8% for Cu-AAO-9 h and 6% for Cu-AAO-12 h at 300°C. Methanol conversion was less for Cu-AAO-12 h though the copper content was high which could be explained because of highly dispersed Cu in the pores of alumina. This resulted in a lower conversion but high selectivity toward H_2 which was ~ 80%.

The Cu-AAO-HWT catalysts showed higher conversion for less Cu content as the active Cu was concentrated in the top layer (~2 μm). Though the conversion was high, the selectivity to H_2 is less due to the formation of dimethyether (DME) at 275°C for Cu-AAO-HWT-30 m and Cu-AAO-HWT-60 m and at 230°C for Cu-AAO-HWT-90 m. Similar effect was observed when Cu-AAO was prepared with 0.5 and 1.0 M molar Cu $(NO_3)_2$ solution, (i.e., with high concentration) as this resulted in the formation of bulk copper on the surface with 5 Cu wt%. Nearly 75% of methanol was converted but H_2 selectivity was dominated by DME which was not the desired reaction.

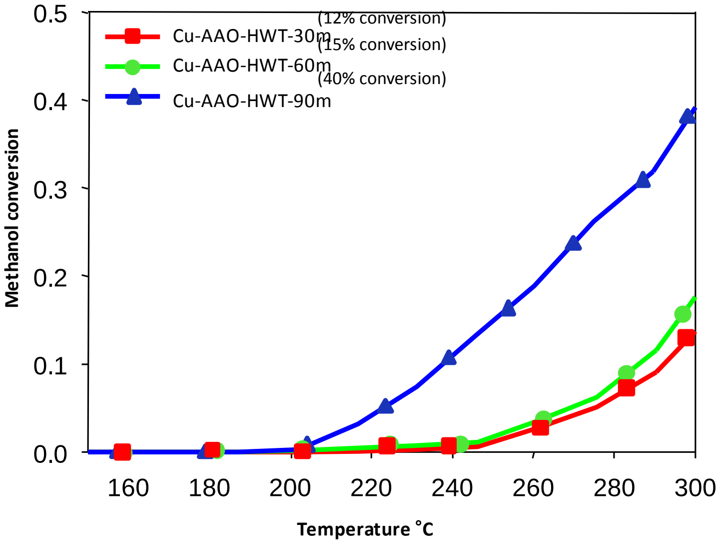


Fig. 1: *Conversion of Methanol over Cu-AAO-HWT Catalysts.*

As it can be seen from the SEM images (in characterization section) with increase in dipping time, the amount of copper deposited into pores as well as on the surface increases and as a result, the surface of the catalyst is covered by bulk copper species blocking the pores of the catalyst and thereby decreasing the activity. To avoid this, dipping method has been modified by reducing the dip time to 1 h and increasing the number of dipping (successive dipping method). After each dipping, the samples are dried and calcined and the experiment is repeated for five times. The activity of catalysts prepared by this method is shown in Figure 2(a). From Figure 2, it can be observed that with each dipping the conversion has increased from 8% for Cu-AAO-1 to 73% for Cu-AAO-5. To check the effect of zinc on the activity, the Cu-AAO-5 catalyts has been impregnated with Zn by dipping this in 0.25M zinc nitrate solution for 1h and the activity has increased giving a conversion of 97%. To further study the effect of Cu and Zn, Cu-Zn-AAO catalysts has been prepared (as described in experimental section) and its activity was studied (Figure 2(b)). The combination of copper and zinc has proved to be good as compared to Cu-AAO catalyst.

Characterization

The surface morphology analysis showed uniform pore formation at the optimum conditions of 6 h anodization in 0.3 M oxalic acid at 25°C with a pore size of 50 nm and 50 μm thickness as shown in Figure 3 (AAO). The BET surface area has been found to be 6.75 m^2/g-AAO. Similarly, SEM morphology of AAO-HWT can be seen which shows a change in surface as the Al_2O_3 structure is transformed to hydrated alumina. Also at the HWT conditions only the top layer (~2 μm) of the AAO film is hydrated and the rest of the film retains its porous structure as can be seen in the cross-sectional image. However there was a large improvement in the surface area which was 71.5 m^2/g-AAO.

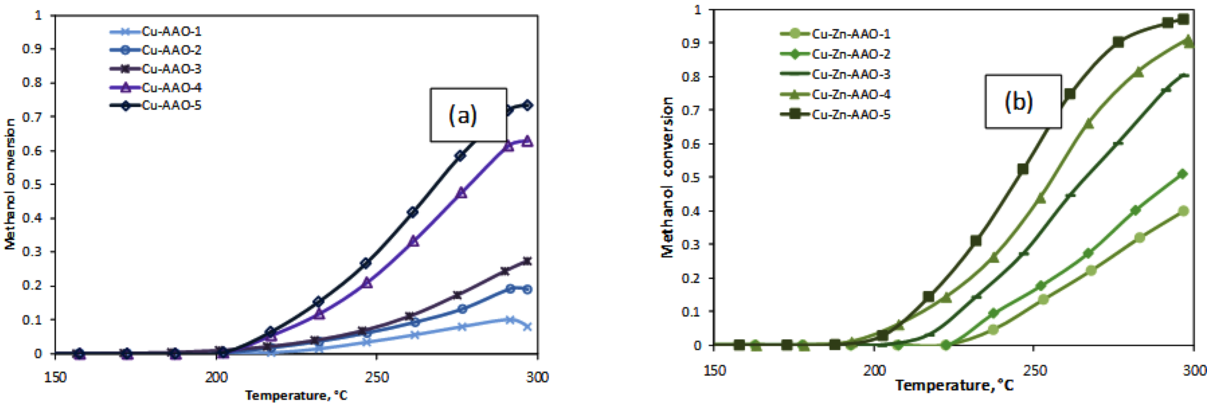
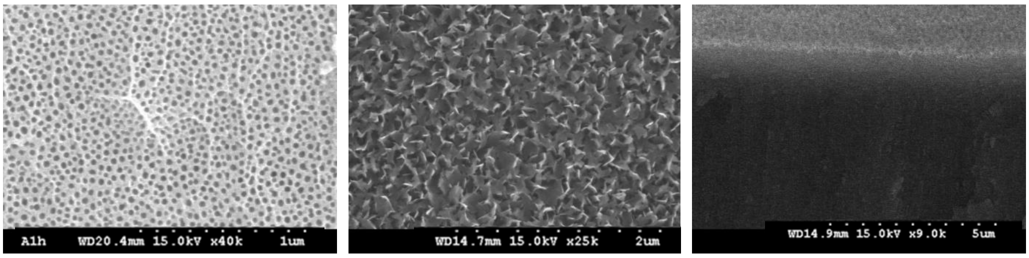


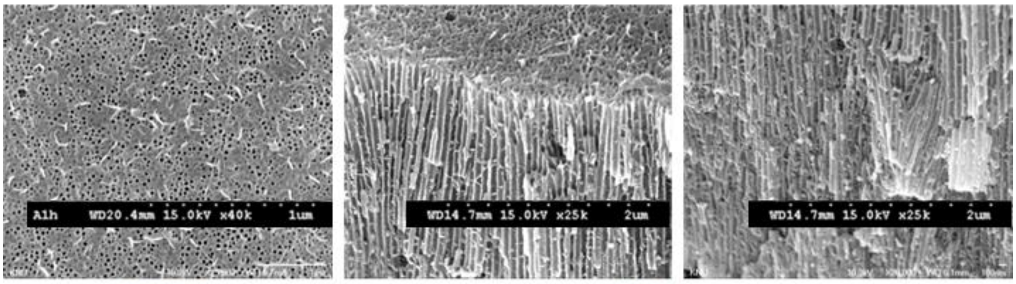
Fig. 2: *Conversion of Methanol over Cu-AAO and Cu-Zn-AAO Catalysts.*



AAO **AAO-HWT** **AAO-HWT-Crosssection**

Fig. 3: *FE-SEM Morphology of AAO and Hot Water Treated AAO (AAO-HWT).*

The SEM analysis of Cu-AAO catalyst is also shown in Figure 4 which confirms impregnation of Cu in the pores of alumina throughout the film. From EDAX analysis a Cu wt% of 3, 8 and 12 has been observed for Cu-AAO-3h, Cu-AAO-9h and Cu-AAO-12h catalysts, respectively. For the Cu-AAO-HWT catalysts, a Cu wt% of 2.8, 3.2 and 6.5 for Cu-AAO-HWT-30 m, Cu-AAO-HWT-60 m and Cu-AAO-HWT-90 m, respectively was observed. Though Cu-AAO catalysts were impregnated for longer time compared to Cu-AAO-HWT catalysts, the higher Cu content can be explained by the increased surface area on hydrated catalysts and its effect on catalytic activity can be observed in next section. Cu-AAO-5 has a Cu content of 2.4 wt% which is less but gave more conversion that the above catalysts due to high dispersion of active metal. This can also be justified from the XRD profiles of the catalysts shown in Figure 5. The Cu-AAO-12h catalyst shows strong peaks of Cu and CuO indicating the presence of bulk species on the surface. The Cu-AAO-HWT XRD profile shows only one peak for Cu and the Al and Al_2O_3 peaks are suppressed due to HWT. The Cu-AAO-5 h XRD profile also shows single peak for Cu with dominant Al and Al_2O_3 peaks. A broad peak at 30 deg represents amorphous and dispersed Cu on the surface.



Surface **Cross section**

Fig. 4: *FE-SEM Morphology of Copper Impregnated Catalysts.*

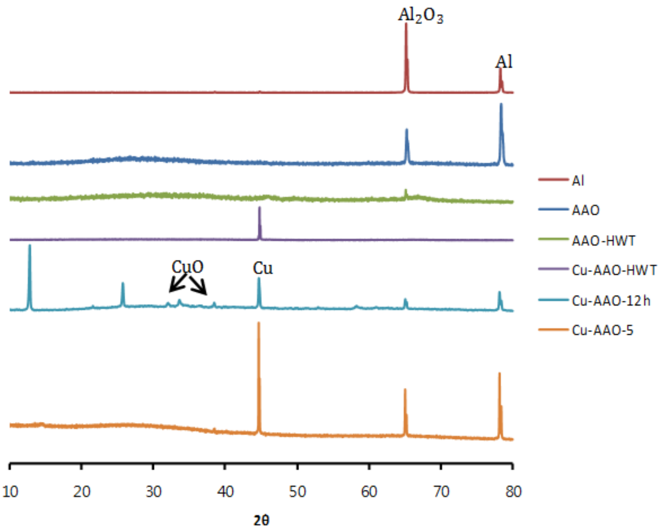


Fig. 5: *XRD Pattern of Al, AAO, AAO-HWT and Copper Impregnated Catalysts.*

IV. CONCLUSION

Hydrogen production by methanol steam reforming (MSR) is easy and simple as compared to other reforming methods using fossil fuels such as methane steam reforming. The catalysts for MSR are well developed and available commercially. When constructing a small or micro reformer, the catalyst often needs to be coated on the wall of the metal substrate. In this case, the bonding between the metal surface and the catalyst layer must be strong enough to avoid peeling of the layer. Simple catalyst slurry coating on the metal surface has not been successful due to the inherent weak bonding between the metal and the metal oxide layer. In this study, to develop a robust catalyst layer, we first formed a strongly bonded porous aluminum oxide layer on an aluminum metal surface and then impregnated it with an active metal, Cu. Copper metal is incorporated into the pores of alumina by impregnation using different concentrations of copper nitrate solution (Cu-AAO). The surface morphology of the catalysts has been monitored by FE-SEM at various stages of synthesis and the amount of Cu metal incorporated has been analyzed by SEM-EDX. This paper discusses the development of Cu-AAO catalyst for methanol steam reforming.

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