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Steam Reforming of Methanol Over $Cu/Al_2O_3/ZnO$ Catalysts

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In this research, steam reforming of methanol over $Cu/Al_2O_3/ZnO$ catalysts was investigated. The catalysts were prepared by conventional co-precipitation and sequential precipitation methods. Especially, the sequential precipitation method were performed by varying the sequence of additions of copper, aluminum, and zinc nitrate solutions. The experimental results showed clearly that the preparation methods affected the performance of catalysts. The $Cu/Al_2O_3/ZnO$ catalysts prepared by consecutively adding copper, aluminum, and zinc nitrate solutions exhibited better performance. The effect of Al_2O_3/ZnO molar ratios on the activity of catalysts was also studied. It was found that the catalysts with 50:5:45 of $Cu/Al_2O_3/ZnO$ molar ratio showed higher activity than others. In order to improve catalytic activity, Mn- or Cr-promoted over $Cu/Al_2O_3/ZnO$ was also investigated. It was interesting to observe that either the Mn- or the Cr-promoted $Cu/Al_2O_3/ZnO$ catalysts have higher activity than nonpromoted ones, indicating that Mn and Cr promoters give some synergistic effect.

INTRODUCTION

During the last twenty years, there has been significant worldwide interest in finding methods to reduce emission from mobile sources, especially internal combustion engines. One possibility is to use a fuel cell-powered vehicle using hydrogen as fuel. However, the disadvantage of hydrogen is its being a the low density gas under normal condition, leading to storage and transportation problems. Accordingly, a promising way of steam reforming of methanol to produce hydrogen has attracted many researchers to pay more attention.

Due to the high activity of copper-based catalysts for methanol synthesis, majority of researches (Akaratiwa, 2000; Jiang, 1993; Shen, 1997) have focused on the steam reforming of methanol over these catalysts. The active catalysts for this reaction operates at a temperature low enough that carbon monoxide, which is a potential poison for a typical platinum-catalyzed solid polymer fuel cell, is not a significant product but is stable when operating conditions have been developed continuously. Raphael O. Idem, et al. (1995) reported that the promotion of coprecipitated Cu/Al catalysts with Mn and Zn results in enhancement of methanol conversion in methanol steam reforming reaction, while Wu-Hsun Cheng, et al. (1998) found that the activity of Cu/Cr/Mn catalysts for decomposition of methanol to CO and H_2 can be enhanced by adding small amounts of alkali additives. Consequently, there were also attempts to improve Cu/ZnO catalysts for methanol-steam reforming by promoting such metals in the previous studies (Akaratiwa, 2000; 2001). Unfortunately, the modified catalysts, however, did not produce the desired high catalytic performance. According to

John P. Breen, et al. (1999), the addition of alumina to Cu/ZnO exhibited synergistic behavior and increased activity, but the effect of preparation methods in different sequence addition of metal nitrate salts was not investigated. Therefore, the main aim of this research is to describe the development of $Cu/ZnO/Al_2O_3$ for steam reforming of methanol. The activity of unpromoted $Cu/ZnO/Al_2O_3$ catalysts with various Al_2O_3/ZnO molar ratios prepared either by sequential precipitation (SP) in different sequence addition of metal nitrate salts or coprecipitation (CP) of the metal nitrate salts using sodium bicarbonate as the precipitants were studied. The effect of incorporating oxides of Mn and Cr promoters into $Cu/Al_2O_3/ZnO$ catalysts were also studied.

EXPERIMENTAL

Catalyst preparation

The nonpromoted $Cu/ZnO/Al_2O_3$ catalysts were prepared by conventional coprecipitation (CP) and sequential precipitation (SP) in various molar composition. In case of coprecipitation method, a mixed $Cu(NO_3)_2/Zn(NO_3)_2$ solution (1.0 M) was added dropwise to $NaHCO_3$ solution used as precipitant at a constant temperature of 65°C with stirring. To ensure that all components can precipitate completely, the stoichiometric amount of $NaHCO_3$ was used. In case of sequential precipitation, the catalysts were prepared with different sequence addition of metal nitrate solutions. For example, the $Cu/ZnO/Al_2O_3$ (SP) catalyst was prepared by precipitating copper, then aluminium, and zinc, consecutively. The precipitates were then aged for 60 min under continuous stirring, then filtered, washed with deionized water, dried at 105°C overnight, and followed by calcination in air at 350°C for 4h.

For the Cr or Mn promoted $Cu/Al_2O_3/ZnO$ catalysts, the sequential precipitates either before or after calcination were used as precursors. 0.32% of Mn or Cr were incorporated into these dried catalyst precursors by impregnation using aqueous solutions of manganese nitrate and chromium nitrate. Then, these promoted catalysts were dried at 105°C overnight, and followed by calcination in air at 350°C for 4h.

Catalytic activity test

Prior to activity test, 400 mg of catalysts were loaded into a micro-reactor, pretreated at 350°C in the air and then reduced in 3% H_2 atmosphere balanced with N_2 at a flow rate of 100 ml/min at 250°C for 1h. The catalytic reaction was carried out at atmospheric pressure in a conventional flow system over a temperature range of 150 to 350°C. The mixture of water and methanol in 1:2 of water-to-methanol molar ratios was introduced into the micro-reactor by micro-feeder and rapidly vaporized into N_2 stream before entering the catalyst bed. The total inlet flow rate was kept at 100 ml/min. The reactants and products in the outlet stream were analyzed by gas chromatography with a thermal conductivity detector.

RESULTS AND DISCUSSION

The effect of preparation methods

Fig.1 compares the activities of catalysts prepared by co-precipitation and sequential precipitation ($Al_2O_3/Cu/ZnO$; first, aluminum; then copper and zinc, consecutively) with various molar ratios of Al_2O_3 to Al_2O_3+ZnO but containing the same molar of copper. The temperature chosen for the comparisons was 250°C. The results show clearly that the sequential precipitation prepared catalysts have higher activities than of those with the same composition prepared by coprecipitation. The reasons for these differences will probably be due to the noticeable textural and structural properties of those catalysts which were reported by J.P. Breen, et al. (1999). The effect of compositions on the performance of catalysts prepared either by coprecipitation or sequential precipitation was also observed. Maximum conversion of methanol was found at 0.5 molar ratio of Al_2O_3 to $Al_2O_3 + ZnO$ in both catalysts prepared by different methods.

The effect of addition sequence of metal nitrate solutions

The catalysts prepared by SP show higher performance than those prepared by CP. To verify whether the addition sequence of metal nitrate solutions during catalyst preparation would be influential in the activity of catalysts, many

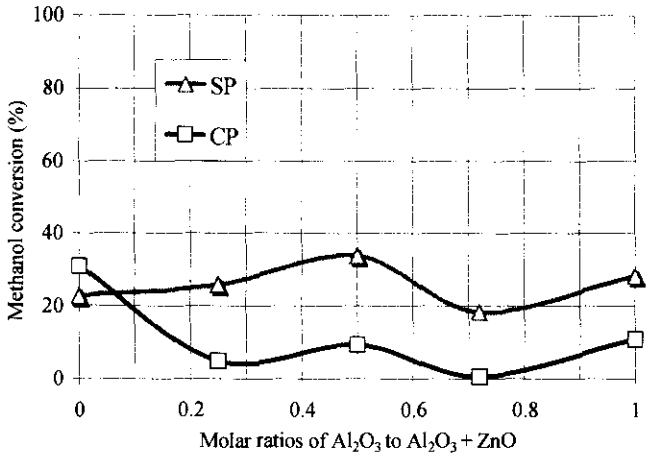

Figure1. The influence of molar ratios of Al_2O_3 to Al_2O_3 + ZnO on methanol Figure1. The influence of molar ratios of Al_2O_3 to Al_2O_3 + ZnO on methanol conversion over Al_2O_3/Cu/ZnO catalysts prepared by sequential precipitation (Δ) and co-precipitation (□)

samples were prepared. Figs. 2 [a], [b] and [c] show activity test results of the SP catalysts of which Zn, Cu, and Al precipitated in the last order, respectively. From the results, the effect of addition sequence on the performance of the SP catalyst of which Zn precipitated in the last order was observed to be different (Fig. 2 [a]), and scarcely different activities in the SP catalysts of which Cu and Al precipitated in the last order (Figs. 2 [b] and [c]). Expectedly, latter was probably due to the differences in the local composition of the catalysts. However, further investigation of catalyst structure would be necessary. The results also showed that methanol conversion for the SP catalysts of which Zn precipitated in the last order was within 50 to 70 % at 300°C, and about 40% for those of which Cu or Al precipitated in the last order, which indicated that $Cu/Al_2O_3/ZnO$ catalysts, were superior to those whose active species of Cu precipitated on Al and Zn precipitates. The performance of Cu-impregnated Al_2O_3/ZnO catalysts (dotted line in Fig 2. [b]) was also compared with that of $Al_2O_3/ZnO/Cu$ catalyst, but exhibited almost the same activity.

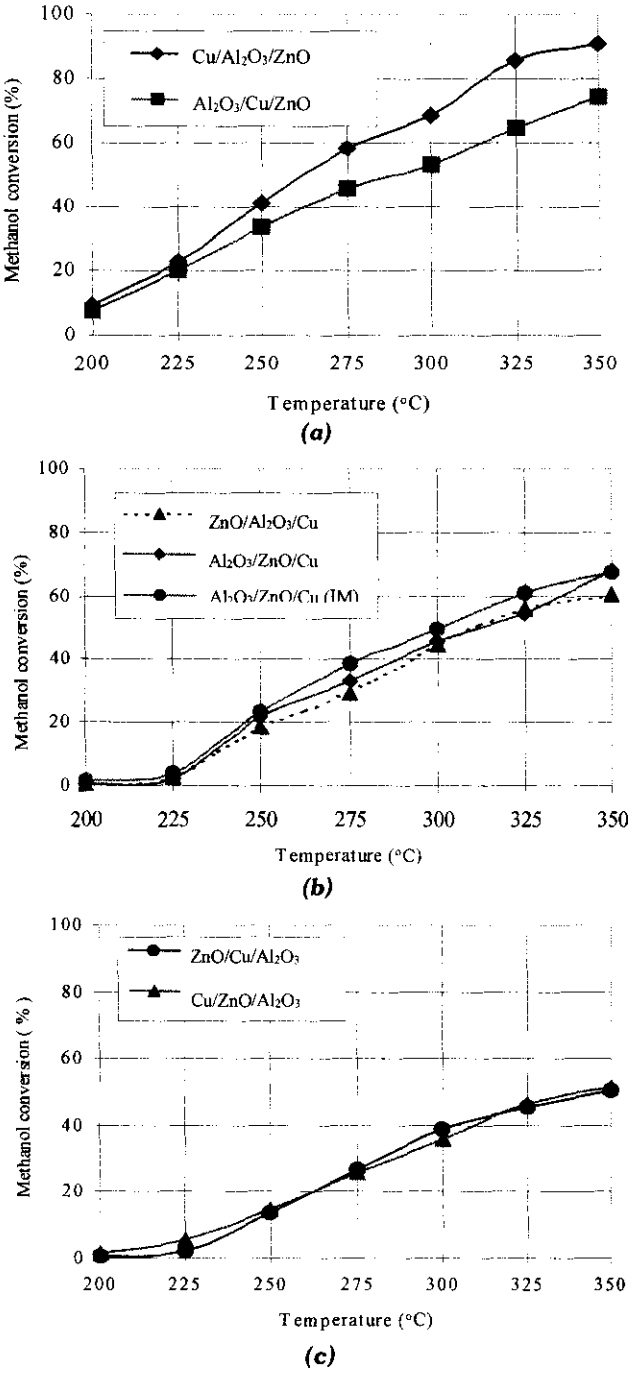

Figure 2. Performance of the SP catalysts prepared by different addition sequence of metal nitrate solutions of which (a) Zn (b) Cu and (c) Al precipitated in the last order in term methanol conversion

The effect of molar ratios of Al_2O_3 to Al_2O_3 + ZnO in $Cu/Al_2O_3/ZnO$ catalysts

Since the molar ratios of Al_2O_3 to Al_2O_3 + ZnO in $Al_2O_3/Cu/ZnO$ catalysts described in 3.1 affected the performance of catalysts, the same phenomena probably occurred in case of the best $Cu/Al_2O_3/ZnO$ catalysts. To verify this hypothesis, $Cu/Al_2O_3/ZnO$ catalysts with various molar ratios of Al_2O_3 to Al_2O_3 + ZnO but containing the same molar of copper, were tested at 300 and 250°C. Both (Fig. 3) demonstrated the same pattern curve, giving the maximum methanol conversion at 50:5:45 of $Cu/Al_2O_3/ZnO$ molar ratio (or 0.1 of molar ratio of Al_2O_3 to Al_2O_3 + ZnO). However, the proportional relationship between methanol conversion and molar ratios of Al_2O_3 to Al_2O_3 +

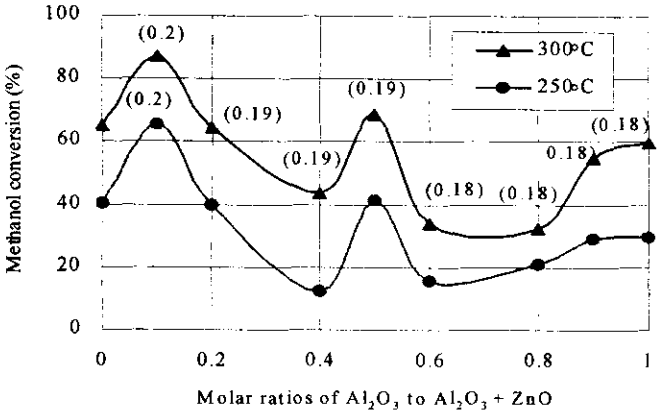

Figure 3. The influence of molar ratios of Al_2O_3 to Al_2O_3 + ZnO on methanol conversion over $Cu/Al_2O_3/ZnO$ catalysts at 300°C (D) and 250°C (o). (Numbers in parentheses are the weight of CuO in 0.4g of used catalysts.)

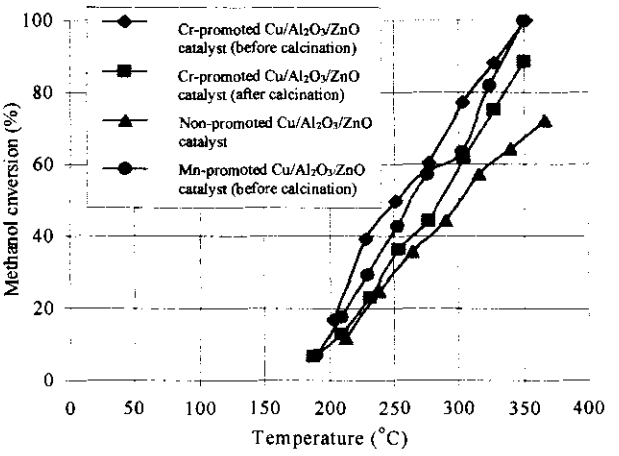

Figure 4. Methanol conversion of non-promoted $Cu/Al_2O_3/ZnO$ catalyst and Cr- or Mn-promoted $Cu/Al_2O_3/ZnO$ catalysts as a function of reaction temperatures

ZnO were not observed, and would need further investigation.

The effect of incorporating oxides of Mn and Cr promoters

Fig. 4 shows the performance of the Cr- and Mn-promoted $Cu/Al_2O_3/ZnO$ catalysts in terms of methanol conversion. Results showed clearly that the activities of promoted catalysts were superior to that of the non-promoted one. The synergistic behavior in promoted catalysts was attributed to the presence of $CuMnO_2$ and $Cu_2Cr_2O_4$ species resulting in increased amounts of copper in the +1 oxidation state. This reaction means an increase in the electron-accepting potential of copper or the redox ability of catalysts and, consequently, an increase in the oxidation of methanol to CO_2. The presence of Cu^{+1} species in Mn-promoted $Cu/Al_2O_3/ZnO$ catalysts was also confirmed by the XRD technique as shown in Fig. 5. Furthermore, it was interesting to observe that the promoted catalysts prepared by impregnating promoters on top of precipitates before calcination were more active than those promoted after calcination.

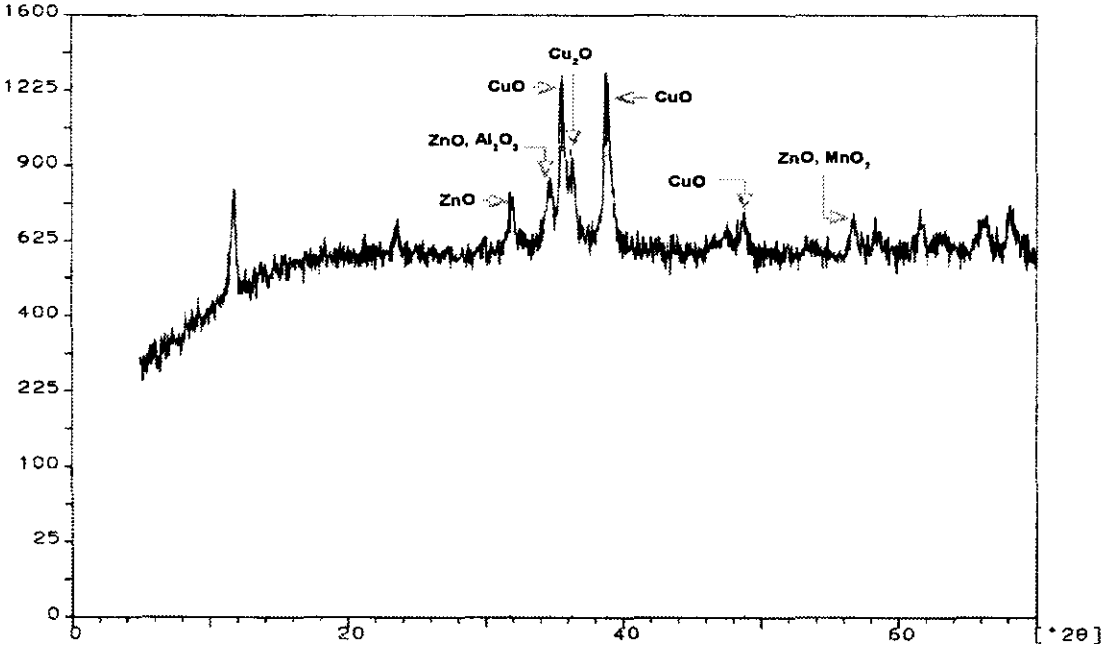

Figure 5. XRD pattern of Mn-promoted $Cu/Al_2O_3/ZnO$

CONCLUSIONS

$Cu/Al_2O_3/ZnO$ catalysts prepared by sequential precipitation by first precipitating copper, and then aluminium and zinc, consecutively, showed higher activity for steam reforming of methanol than those prepared by co-precipitation or other addition sequence of metal nitrate solution. The Al_2O_3/ZnO molar ratios in $Cu/Al_2O_3/ZnO$ catalysts also affected the performance of catalysts. It was found that the catalysts with 50:5:45 of $Cu/Al_2O_3/ZnO$ molar ratio showed higher activity than others. However, the molar ratios of Al_2O_3 to Al_2O_3 + ZnO was found to have no correlation with the methanol conversion. In addition, $Cu/Al_2O_3/ZnO$ catalysts could also be improved by promoting with Mn or Cr.

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