Korean J. Chem. Eng., **19**(1), 17-19 (2002)

Optimum Washing Conditions for the Preparation of Cu/ZnO/ZrO_2 for Methanol Synthesis from CO Hydrogenation: Effects of Residual Sodium

Young-Woong Suh and Hyun-Ku Rhee†

School of Chemical Engineering and Institute of Chemical Processes,
Seoul National University, Kwanak-ku, Seoul 151-742, Korea

(*Received 2 July 2001 • accepted 28 July 2001*)

Abstract–The residual sodium in the Cu/ZnO/ZrO_2 catalyst is found to inhibit the interaction between CuO and ZnO and lead to a decrease in the catalytic activity for CO hydrogenation. Therefore, it is required to reduce the content of sodium as much as possible during the course of catalyst preparation. To obtain 10% yield of methanol, the sodium content must be reduced to a level lower than 0.15%. For this purpose, the washing condition has been investigated experimentally to optimize the preparation conditions of Cu/ZnO/ZrO_2 catalyst. As a result, the sodium content could be reduced to 0.115% by washing the cake four times with 50 mL of distilled water per gram of the cake, which constitutes the optimum condition for washing.

Key words: Cu/ZnO/ZrO_2, Methanol Synthesis, Washing Condition, Sodium Content, CO Hydrogenation

INTRODUCTION

Effective synthesis of methanol has been investigated during the past decades since methanol is considered to be one of the materials that can overcome the forthcoming shortage of petroleum. Methanol is industrially produced from synthesis gas (H_2/CO/CO_2) and the methanol synthesis process is operated at low pressure and temperature using the catalysts containing copper and various oxides such as ZnO and Al_2O_3 [Saito et al., 1997; Lee and Lee, 1995; Lee et al., 2000].

A conventional preparation method of catalyst precursors is the coprecipitation of metal salts by using a basic precipitating agent, most commonly sodium bicarbonate. In general, the precipitates are washed thoroughly with distilled water to remove the residual sodium left in the precipitates, but the complete removal is known to be a rather difficult task.

Recently, Wu et al. [1998] reported that washing of the precipitates to remove the sodium is the most important step in the preparation of highly active catalysts. Also, Jun et al. [1998] examined the relation between the residual sodium and the catalytic activity in CO_2 hydrogenation. According to their results, the residual sodium inhibited the interaction of CuO with ZnO and Al_2O_3 to result in an increase in the crystallinity of CuO and ZnO, and thus decreased the catalytic activity as a result of poor Cu-dispersion. On the basis of these studies, it is evident that the removal of sodium has a direct influence on the methanol synthesis activity. However, the method to remove the residual sodium has not been well studied.

We have prepared Cu/ZnO/ZrO_2 catalysts using different volumes of distilled water and different washing frequencies, and examined the relationship between the content of residual sodium and the catalytic activity for methanol synthesis by the hydrogenation of CO. This article aims for the optimization of the washing condition for the preparation of Cu/ZnO/ZrO_2 catalyst.

EXPERIMENTAL

All the catalysts were prepared by the coprecipitation method. An aqueous solution of copper, zinc and zirconium nitrates having the molar ratio of Cu : Zn : Zr=1 : 2.333 : 0.656 was added to an aqueous solution of sodium bicarbonate at 343 K over a period of 20 min with stirring. The precipitate formed was further aged under stirring for 90 min at the same temperature and then filtered. Subsequently, the cake obtained was washed with distilled water by using different washing techniques. For convenience, the cakes washed with 0.6, 1.8 and 3.0 L of distilled water while other preparation conditions remained the same were designated as Cat1, Cat2 and Cat3, respectively. The cakes washed with 3.0 L of distilled water two, three and four times were referred to as Cat4, Cat5 and Cat6, respectively. All the washed cakes were dried in air at 383 K overnight and calcined in air at 623 K for 12 h.

Reaction was conducted in a fixed-bed reactor heated by a furnace. Prior to all the experiments, calcined catalysts were reduced in pure H_2 at a flow rate of 50 ml/min at 523 K under atmospheric pressure for 3 h. The hydrogenation of CO was then carried out at 523 K by feeding a gas mixture of H_2 and CO with the molar ratio of H_2/CO=4 under a total pressure of 3.45 MPa.

RESULTS AND DISCUSSION

In this study, each of the catalysts tested was prepared from a cake of 60 g. The cakes were then washed with different volumes of distilled water or with different frequencies of operation before drying and calcination to give six different catalysts. These are listed in Table 1 with their washing conditions and Na content.

Fig. 1 shows the experimental results of methanol synthesis by CO hydrogenation over Cu/ZnO/ZrO_2 catalysts with different Na contents. With increasing Na content, the methanol selectivity is maintained fairly constant while the CO conversion gradually de-

---

†To whom correspondence should be addressed.
E-mail: hkrhee@snu.ac.kr

Table 1. Sodium content of $Cu/ZnO/ZrO_2$ catalysts treated under various washing conditions

Catalyst[1]	Volume of distilled water (mL)	Number of washing	Na content (wt%)
Cat1	600	1	12.042
Cat2	1800	1	1.755
Cat3	3000	1	1.126
Cat4	3000	2	0.436
Cat5	3000	3	0.216
Cat6	3000	4	0.115

[1] Weight of cake for each catalyst: 60 g

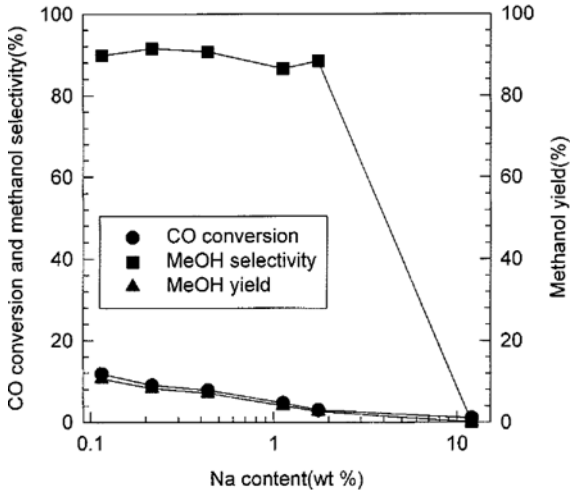

Fig. 1. CO conversion, methanol selectivity and methanol yield as a function of Na content.

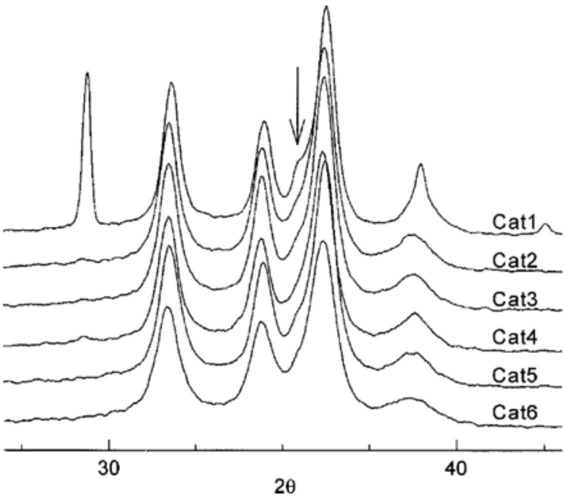

Fig. 2. XRD patterns of $Cu/ZnO/ZrO_2$ catalysts treated under various washing conditions; (•) $NaNO_3$.

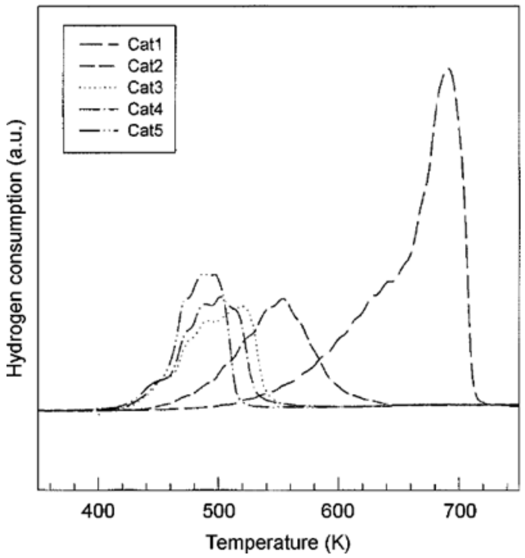

Fig. 3. TPR profiles of $Cu/ZnO/ZrO_2$ catalysts treated under various washing conditions.

creases when the Na content remains lower than ca. 1.7 wt%. Beyond this level of Na content, however, the methanol selectivity is found to decrease rapidly, and practically no methanol is synthesized when the Na content becomes higher than 10 wt%. This indicates that the catalytic activity is closely related to the Na content. In other words, the presence of Na that causes the separation of CuO and ZnO can suppress the synergistic effect between CuO and ZnO and decrease the catalytic activity. Therefore, it is important to remove the residual sodium from the catalyst during the course of catalyst preparation. In particular, the sodium content must be reduced to a level lower than 0.15% to obtain 10% yield of methanol.

We performed the XRD analysis of calcined catalysts to examine any changes in the crystal phases caused by the difference in the Na content. As presented in Fig. 2, broad peaks are observed in all the spectra because CuO and ZnO are well mixed. In particular, the diffraction peaks of CuO and ZnO are overlapped in the range $35^\circ<2\theta<37^\circ$. This represents the well-mixed nature as well as the incorporation of CuO into ZnO. In the catalyst having a high Na content (Cat1), however, there appears a distinct shoulder at $2\theta=35.50^\circ$ and a new sharp peak appears at $2\theta=29.40^\circ$. The former indicates that CuO and ZnO tend to be separated as the Na content increases and the latter peak corresponds to the $NaNO_3$ phase as reported in the literature [Wu et al., 1998; Jun et al., 1998]. It is speculated that this phase may suppress the formation of mixed oxide of CuO and ZnO, and hence the residual sodium in a large content inhibits the interaction between CuO and ZnO.

The TPR profiles from the catalysts with different Na contents are presented in Fig. 3. This figure clearly shows that the catalyst with a low Na content is reduced at a temperature lower than that of pure CuO, which is about 690 K. As the Na content becomes lower, the reduction peak tends to shift to the lower temperature range. It has been reported that such a shift is caused by the synergistic effect between CuO and ZnO and the metal-support interaction (MSI) of Al_2O_3 [Kanai et al., 1996; Nakamura et al., 1995, 1996; Li and Inui, 1996]. Therefore, it may be concluded that the presence of sodium nitrate inhibits the reduction of CuO to Cu^0.

With the understanding that the residual sodium has to be removed as much as possible, we return to the washing conditions given in Table 1. Here it is to be noticed that as a result of increasing the volume of distilled water, the Na content was considerably decreased to about one tenth of that of the catalyst washed with 0.6 L of distilled water. When the cakes were washed repeatedly with 3 L of distilled water, a substantial decrease in the Na content was again observed. Indeed, the catalyst washed four times with 3 L each of distilled water (Cat6) contained only one tenth of Na compared to the catalyst washed only once (Cat3).

According to Jun et al. [1998], a sodium-free sample could be obtained only after ten times of washing. The above results indicate that, for an effective removal of residual sodium, the cakes must be washed not only with a sufficient volume of distilled water but also repeatedly. The experimental result of this study showed that the residual sodium could be reduced to 0.115% by using 50 mL of distilled water per gram of cake for washing and repeating the same procedure four times. It is to be emphasized that this strategy of washing is the optimized one after a number of trials.

CONCLUSIONS

The residual sodium in $Cu/ZnO/ZrO_2$ exercises a significant influence on the catalytic activity for CO hydrogenation. The results of XRD and TPR analyses show that the residual sodium brings about the formation of $NaNO_3$ phase that suppresses the formation of mixed oxide of CuO and ZnO. Therefore, it is evident that the residual sodium inhibits the interaction between CuO and ZnO and leads to a decrease in the catalytic activity. In this study, it is demonstrated that, for an effective removal of residual sodium, the cakes should be washed with a sufficient volume of distilled water repeatedly. To obtain 10% yield of methanol, the sodium content must be reduced to a level lower than 0.15%, and this can be achieved by washing the cake four times with 50 mL each of distilled water per gram of cake.

REFERENCES

Jun, K.-W., Shen, W.-J., Rao, K. S. R. and Lee, K.-W., "Residual Sodium Effect on the Catalytic Activity of $Cu/ZnO/Al_2O_3$ in Methanol Synthesis from CO_2 Hydrogenation," *Appl. Catal. A*, **174**, 231 (1998).

Kanai, Y., Watanabe, T., Fujitani, T., Uchijima, T. and Nakamura, J., "The Synergy between Cu and ZnO in Methanol Synthesis Catalysts," *Catal. Lett.*, **38**, 157 (1996).

Lee, K. H. and Lee, J. S., "Effects of Catalyst Composition on Methanol Synthesis from CO_2/H_2," *Korean J. Chem. Eng.*, **12**, 460 (1995).

Lee, J. S., Han, S. W., Kim, H. G., Lee, K. H. and Kim, Y. G., "Effects of Space Velocity on Methanol Synthesis from $CO_2/CO/H_2$ over $Cu/ZnO/Al_2O_3$ Catalyst," *Korean J. Chem. Eng.*, **17**, 332 (2000).

Li, J.-L. and Inui, T., "Characterization of Precursors of Methanol Synthesis Catalysts, Copper/Zinc/Aluminum Oxides, Precipitated at Different pHs and Temperatures," *Appl. Catal. A*, **137**, 105 (1996).

Nakamura, J., Nakamura, I., Uchijima, T., Kanai, Y., Watanabe, T., Saito, M. and Fujitani, T., "Methanol Synthesis over a Zn-deposited Copper Model Catalyst," *Catal. Lett.*, **31**, 325 (1995).

Nakamura, J., Uchijima, T., Kanai, Y. and Fujitani, T., "The Role of ZnO in Cu/ZnO Methanol Synthesis Catalysts," *Catal. Today*, **28**, 223 (1996).

Saito, M., Takeuchi, M., Watanabe, T., Toyir, J., Luo, S. and Wu. J., "Methanol Synthesis from CO_2 and H_2 over a Cu/ZnO-based Multicomponent Catalyst," *Energy Convers. Mgmt.*, **38**(Suppl.), S403 (1997).

Wu, J., Luo, S., Toyir, J., Saito, M., Takeuchi, M. and Watanabe, T., "Optimization of Preparation Conditions and Improvement of Stability of Cu/ZnO-based Multicomponent Catalysts for Methanol Synthesis from CO_2 and H_2," *Catal. Today*, **45**, 215 (1998).