Korean J. of Chem. Eng., **12**(1), 36-38 (1995)

CATALYTIC BEHAVIOR OF $YBa_2Cu_3O_{7-x}$ IN THE PARTIAL OXIDATION OF METHANOL TO FORMALDEHYDE

Yang Kook Sun* and Wha Young Lee†

Department of Chemical Engineering, Seoul National University, Seoul 151-742, Korea

(*Received 17 February 1994 • accepted 24 September 1994*)

Abstract—The partial oxidation of methanol to formaldehyde was studied over $YBa_2Cu_3O_{7-x}$ catalyst in a flow reactor. The structural change of $YBa_2Cu_3O_{7-x}$ before and after the reaction was measured by means of XRD and iodometric titration method. The catalytic characteristics of $YBa_2Cu_3O_{7-x}$ for the partial oxidation of methanol to formaldehyde was due to copper ions. It was found that Cu^{+2} was responsible for the higher selectivity for formaldehyde.

Key words: *Partial Oxidation of Methanol, Formaldehyde, $YBa_2Cu_3O_{7-x}$ Oxide Superconductor, Iodometric Titration, Copper Valence*

INTRODUCTION

Since it has been disclosed that $YBa_2Cu_3O_{7-x}$ oxide superconductor shows the transition temperature of 90 K, there has been an extensive research effort to study its physical and electrical properties. However, few studies have been done on its catalytic behavior or chemical reactivity. $YBa_2Cu_3O_{7-x}$ is known as the first perovskite family that is composed of copper in its B site of ABO_3 and has an oxygen deficient perovskite structure.

In the viewpoint of catalysis, $YBa_2Cu_3O_{7-x}$ is expected to show a different catalytic behavior from the ABO_3-type perovskites, because $YBa_2Cu_3O_{7-x}$ has less oxygen content than conventional perovskites. For this reason, $YBa_2Cu_3O_{7-x}$ has been studied as a catalyst. It includes the total oxidation and ammoxidation of toluene in the presence of molecular oxygen and ammonia [1], NO decomposition [2, 3], NO reduction by CO [4], CO oxidation [5], the selective oxidation and dehydrogenation of methanol [6], and the partial oxidation of methane [7], and partial oxidation of ethanol [8].

In most cases, it was reported that the superconducting phase was partially decomposed during the reaction [6-9]. Therefore, it is presumed that the resulting stable phases such as Y_2BaCuO_5, $BaCuO_2$, CuO, and Cu metal may be responsible for the catalytic activity.

Considering the oxygen deficiency of $YBa_2Cu_3O_{7-x}$, this oxide superconductor can be a candidate for a partial oxidation catalyst, differing from the ABO_3-type perovskites that have been studied as a total oxidation catalyst [10-13]. It was also reported that the oxygen contents of $YBa_2Cu_3O_{7-x}$ were closely related with the oxidation state of copper [8, 14].

In this study, $YBa_2Cu_3O_{7-x}$ has been investigated as a catalyst for the partial oxidation of methanol to formaldehyde. The structural change and the oxidation state of copper, and the oxygen contents in the $YBa_2Cu_3O_{7-x}$ catalysts before and after the reaction were extensively investigated.

EXPERIMENTAL

$YBa_2Cu_3O_{7-x}$ catalyst was prepared by the amorphous citrate process [8, 15, 16] using $Y(NO_3)_3\,5H_2O$ (Aldrich Chem. Co., 99.9 %), $Ba(NO_3)_2$ (Aldrich Chem. Co., 99.99%) and $Cu(NO_3)_2\,3H_2O$ (Fluka Chemika, 99%). A stoichiometric amount of each nitrate salts with cationic ratio of Y : Ba : Cu = 1 : 2 : 3 was dissolved in distilled water and mixed well with an aqueous solution of citric acid. One equivalent gram of citric acid was used for each total equivalent gram of the metals. Ammonia solution was slowly added to the solution at a rate of 2 cc/min with constant stirring until pH of 6 was achieved. The resulting solution was heated at 70-80℃ for 3-4 days until transparent viscous sol was obtained. The resultant sol was dried at 80℃ in a vacuum dryer to yield a gel, which was then decomposed at 500℃ for 2 hours in air to eliminate organics. The decomposed powder was ground and then calcined at 910℃ for 3 hours in air.

The structural change of $YBa_2Cu_3O_{7-x}$ before and after the reaction was confirmed by X-ray diffraction (Rigaku, D-500). The average copper valence and oxygen contents were determined by the iodometric titration method [17]. The surface area of $YBa_2Cu_3O_{7-x}$ catalysts prior to the reaction was measured by BET method and its transition temperature was determined by means of four probe method.

The reaction was performed in a quartz flow reactor with 4 mm I.D. where oxygen was used as a carrier gas. The reaction temperature was measured by a CA thermocouple placed on the surface of catalyst bed and was controlled precisely with a PID controller within ± 1.0℃. 200 mg of catalysts was placed above quartz wool and pretreated at 320℃ in a stream of oxygen.

Methanol was introduced through a microfeeder into oxygen stream and vaporized by the heating coil around the tube at the reactor inlet. The reaction products were analyzed by a gas chromatography (Yanako, G 1800) with Porapack T packing material.

RESULTS AND DISCUSSION

The surface area of $YBa_2Cu_3O_{7-x}$ was 1.0 m^2/g-cat, and its transition temperature was 94 K. Fig. 1 shows the temperature depend-

---

*Present address: Samsung Heavy Industries Co., Ltd. Daeduk R & D Center

†To whom all correspondence should be addressed.

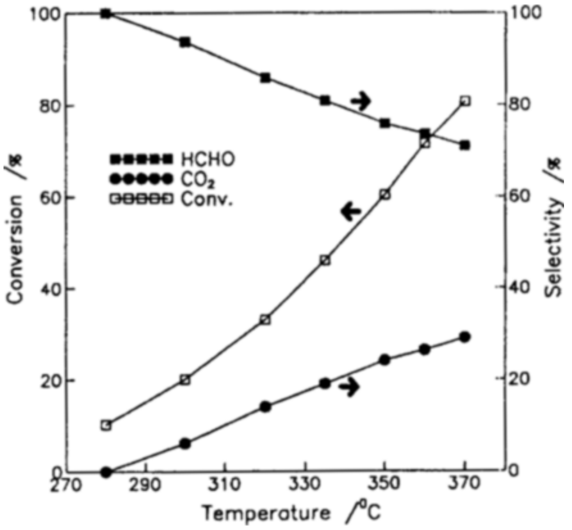

Fig. 1. Conversion or selectivity vs. temperature.
(P_{MTH}=8.8%, F/W=25000 ml/hr·g-cat.)

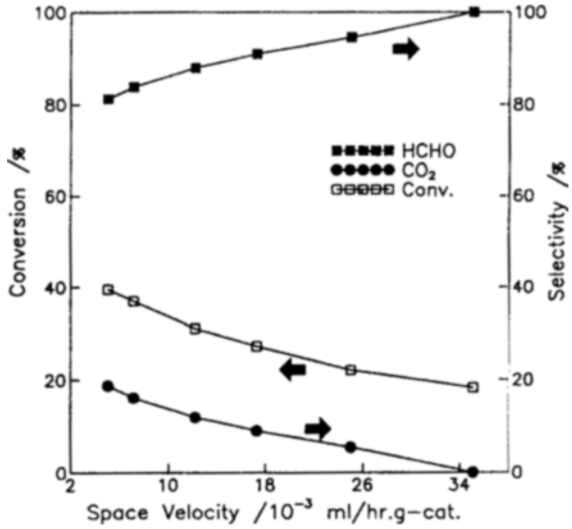

Fig. 2. Conversion or selectivity vs. space velocity.
(P_{MTH}=8.8%, T=300℃)

ence on the methanol conversion and the selectivities for formaldehyde and CO_2. As the reaction temperature increases, the proportion of CO_2 in the products increases. Fig. 2 exhibits the effect of space velocity on the methanol conversion and the selectivities for formaldehyde and CO_2 at the reaction temperature of 300℃. The selectivity for formaldehyde increases linearly with the increase of space velocity, while that for CO_2 decreases. When the space velocity was more than 35000 ml/hr·g-cat, the reaction product was only formaldehyde. The tendency of conversion is similar to cobalt based perovskites [18], although an exact comparison of the activites is not possible because of the different reaction conditions. Nonetheless, a signifinicant difference appeared in the product distribution: Formaldehyde was the main product containing CO_2 and H_2O on $YBa_2Cu_3O_{7-x}$ catalyst, while only CO_2 and H_2O were formed from on cobalt based perovskites. The selective formation of formaldehyde is a characteristics of metallic copper [19, 20]. In order to investigate the catalytic characteristics of $YBa_2Cu_3O_{7-x}$ for methanol to formaldehyde, the fresh catalyst (the catalyst before the reaction) and used catalyst (the catalyst after the reaction) were carefully examined by X-ray diffaraction and iodometric titration. The results of iodometric titration and X-ray diffraction patterns are shown in Table 1 and Fig. 3, respectively.

Table 1. Average copper valence and oxygen contents of the fresh and used $YBa_2Cu_3O_{7-x}$

	Fresh catalysts	Used catalysts
Aaverage copper valence	2.23	2.0
Oxygen contents	6.85	6.5

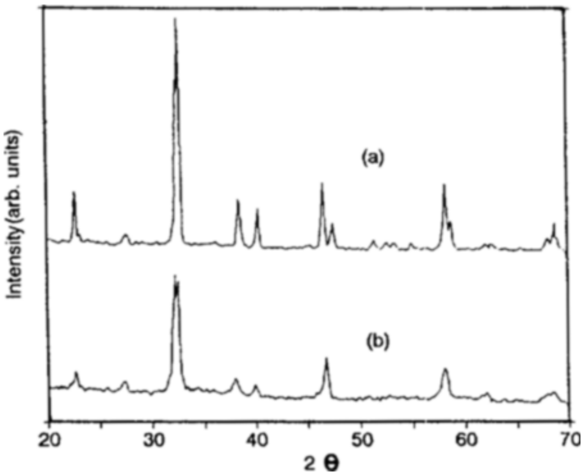

Fig. 3. X-ray power diffraction of $YBa_2Cu_3O_{7-x}$ Catalysts.
(a) before the reaction, (b) after the reaction

From the results of the XRD patterns and iodometric titration of $YBa_2Cu_3O_{7-x}$, it was found that the fresh $YBa_2Cu_3O_{7-x}$ is an orthorhombic structure of a nearly pure phase, where the average copper valence is 2.23 and the oxygen contents is 6.85. However, the used $YBa_2Cu_3O_{7-x}$ showed a pure phase tetragonal structure with the average copper valence is 2.0 and the oxygen contents is 6.5. Other impurity and copper peaks were not observed at all. The difference of XRD patterns between the fresh and the used catalysts can be interpreted from an orthorhombic to a tetragonal phase transition [21]. This result is well consistent with a report [14] that average copper valence decreases with the decrease of oxygen contents and orthorhombic to tetragonal phase transition occurs at the oxygen contents of 6.5.

From above results, it is concluded that the catalytic characterstics of methanol to formaldehyde over $YBa_2Cu_3O_{7-x}$, differentating from conventional perovskites, is the characteristic of Cu in its B site. The average copper valence, for this case, is 2.0.

Fig. 4 exhibits the dependence of time-on-stream on the methanol conversion and the selectivies for formaldehyde and CO_2 at 250℃. The catalytic activity of $YBa_2Cu_3O_{7-x}$ decreases with the reaction time. The selectivity for CO_2 is higher than that for formaldehyde when methanol conversion is 87% (reaction time of 10 min). However, when the methanol conversion is 52% (reaction time of 30 min) the selectivity for formaldehyde becomes higher than that for CO_2. With the increase of time-on-stream the selectivity for formaldehyde increases and the selectivity for CO_2 decreases, and thus the selectivity difference between formaldehyde and CO_2 gets larger along with the decrease of methanol conversion. Steady state activity was attained after about two hours, and no remarkable change was observed during the rest of run. As the

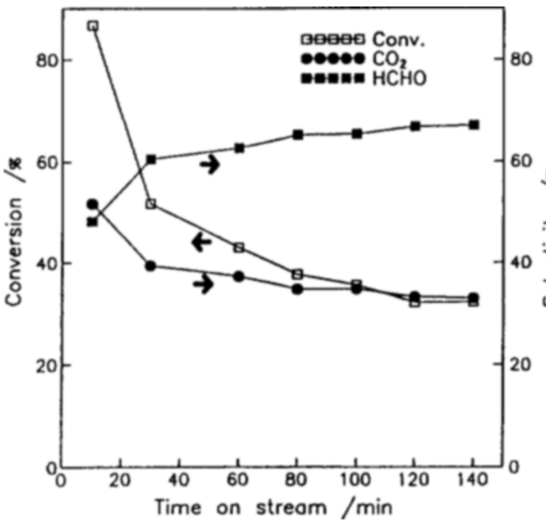

Fig. 4. Conversion or selectivity vs. time on stream.
(T=250℃, F/W=2000 ml/hr·g-cat.)

reaction proceeds, the lattice oxygen is consumed. As a result of lattice oxygen consumption, the oxidation state of copper is changed from Cu^{+3} to Cu^{+2}. As fresh $YBa_2Cu_3O_{6.85}$ having orthorhombic structure has much lattice oxygen to be participated in the reaction, thus, the total oxidation of methanol prevails and methanol conversion becomes higher. On reaching steady state the partial oxidation prevails and methanol conversion becomes lower because $YBa_2Cu_3O_{6.5}$ having tetragonal structure has limited lattice oxygen. The dissociation of lattice oxygen from $YBa_2Cu_3O_{6.5}$ seems to be rather difficult due to the existence of an additional metal-oxygen bond (Ba-O, Y-O) in the stable perovskite structure. Steady state activity appears after the formation of a pure tetragonal $YBa_2Cu_3O_{6.5}$ phase which contains only Cu^{+2} ions and is not able to be reoxygenated below 700℃ [22]. This is well accorded with the results of X-ray diffraction patterns and iodometric titration.

CONCLUSION

$YBa_2Cu_3O_{7-x}$ can partially oxidize methanol to formaldehyde. This is a different catalytic behavior from the conventional perovskite. The catalytic characteristics of $YBa_2Cu_3O_{7-x}$ in the oxidation of methanol were closely related to the oxidation state of copper ions and the lattice oxygen contents. Steady state activity was observed after the formation of pure tetragonal $YBa_2Cu_3O_{6.5}$ phase which contains only Cu^{+2}. It was found that Cu^{+2} was responsible for the high selectivity for formaldehyde.

REFERENCES

1. Hansen, S., Otamiri, J., Bovin, J. O. and Anderson, A.: *Nature*, **334**, 143 (1988).
2. Tabata, K., Fukuda, H., Kochiki, S., Mizuno, N. and Misono, M.: *Chem. Lett.*, 799 (1988).
3. Shimada, H., Miyama, S. and Kuroda, H.: *Chem. Lett.*, 1797 (1988).
4. Mizuno, N., Yamato, M. and Misono, M.: *J. Chem. Soc., Chem. Commun.*, **13**, 887 (1988).
5. Jiang, A. R., Peng, Y., Zhon, Q. W., Gao, P. Y., Yuam, H. Q. and Deng, J. F.: *Catal. Lett.*, **3**, 235 (1989).
6. Halasz, I.: *Appl. Catal.*, **47**, L17 (1988).
7. Lee, I. and Ng, K. Y. S.: *Catal. Lett.*, **2**, 403 (1989).
8. Sun, Y. K. and Lee, W. Y.: *Catal. Lett.*, **17**, 263 (1993).
9. Arakawa, T. and Adachi, G.-Y.: *Mat. Res. Bull.*, **24**, 529 (1989).
10. Kim, J. B., Lee, W. Y., Rhee, H. K. and Lee, H.-I.: *Hwahak Konghak*, **26**(5), 535 (1988).
11. Tak, Y. S., Lee, G. D., Lee, W. Y. and Lee, H.-I.: *Hwahak Konghak*, **26**(6), 641 (1988).
12. Kim, Y. H., Lee, G. D., Lee, W. H., Rhee, H. K. and Lee, H.-I.: *Hwahak Konghak*, **29**(5), 596 (1991).
13. Kim, J. S., Choi, J. H. and Lee, W. H.: *Korean J. of Chem. Eng.*, **9**(1), 45 (1992).
14. Cava, R. J., Batlogg, B., Chen, C. H., Rietman, E. A., Zahurak, S. M. and Werder, D.: *Phys. Rev.*, **B36**, 5719 (1987).
15. Chu, C. T. and Dunn, B.: *J. Am. Ceram. Soc.*, **70**, C375 (1987).
16. Choi, J. S., Sun, Y. K., Jung, S. J. and Lee, W. Y.: *Hwahak Konghak*, **28**(4), 444 (1990).
17. Harris, D. C. and Hewston, T. A.: *J. Solid State Chem.*, **69**, 182 (1987).
18. Nakamura, T., Misono, M. and Yoneda, Y.: *J. Catal.*, **83**, 151 (1983).
19. Huang, T. J. and Chren, C. L.: *Appl. Catal.*, **40**, 43 (1988).
20. Wachs, I. E. and Madix, R. J.: *J. Catal.*, **53**, 43 (1978).
21. Jorgensen, J. D., Beno, M. A., Hinks, D. G., Soderholm, L., Volin, K. J., Grace, J. D., Hitterman, R. L., Schuller, I. K., Segre, C. U., Zhang, K. and Kleefisch, M. S.: *Phys. Rev.*, **B36**, 3608 (1987).
22. Dharwadkar, S. R., Jakkal, V. S., Jakhami, J. V., Gopalakrishnan, I. K. and Iyer, R. M.: *Solid State Commun.*, **64**, 1429 (1987).