

Low-Temperature CO Oxidation Over CuO/Co₃O₄ Catalysts

SULIN HU, TAO CHENG, YOUJIN ZHANG*,
ZHIYONG FANG, KAIDONG HAN and MINRUI GAO
*Department of Chemistry, University of Science and
Technology of China, Hefei, 230026, P. R. China
Fax: (86)(551)3492083; Tel: (86)(551)3492145
E-mail: zyj@ustc.edu.cn*

Copper cobalt composite oxide catalysts have been prepared by co-precipitation method. The prepared samples are characterized by X-ray diffraction, transmission electron microscopy, electron diffraction, X-ray photoelectron spectra and nitrogen adsorption to determine the specific surface areas (S_{BET}). The catalytic activity and stability of samples were investigated for CO oxidation by using a microreactor-GC system. The results indicate that the copper cobalt composite oxide catalysts exhibited obviously higher catalytic activity for CO oxidation than that of individual CuO or Co₃O₄ with CO total conversion at 80 °C and their stability was quite well. The catalytic activity of the catalysts prepared by co-precipitation increases by increasing the calcination temperature from 150 to 200 °C and decreases from 200 to 500 °C. The effect of the volume of NaOH (2.0 mol/L), ageing time, calcination temperature, calcination time, the molar ratios of copper to cobalt and the specific surface areas on the catalytic activity of the catalysts was investigated in this paper.

Key Words: CuO/Co₃O₄ catalysts, CO Oxidation, Catalytic activity, Stability.

INTRODUCTION

At the present time, the low-temperature catalytic oxidation of CO to CO₂ has become an important research topic for its intensive applications, such as air-purification devices for respiratory, gas purification in CO₂ lasers, CO gas sensors and control devices for reducing industrial and environmental emission¹⁻⁴. Precious metal catalysts with high catalytic activity and stability have long been used as the most efficient CO oxidation catalysts⁵⁻⁹. But the availabilities of precious metal catalysts were limited, due to the high cost, sensitivity to sulfur poisoning and needing for complex pre-treatment. Therefore, the base metal and their oxides catalysts, especial transition

metal and their oxides, were extensively researched for the lower cost and significant activities¹⁰⁻¹². Among the base metal and their oxides, copper and copper oxides have been explored as a possible substitute for precious metals for its high catalytic activity for low-temperature CO oxidation¹³⁻¹⁷. Cobalt oxide and other metal oxide-based catalysts, including its composite oxides, show high catalytic activity for low-temperature CO oxidation in CO/O₂ mixtures and have been studied by several groups¹⁸⁻²⁵. Due to the synergistic effect, the composite oxides of transition metal exhibited obviously higher catalytic activity on CO oxidation at low temperature than that of individual transition metal and their oxides²⁶⁻³². Nano-phase transition metal and their oxides may potentially provide significantly improved catalytic activities over non-nano catalysts, due to their small particle size, high specific surface area and perhaps more significantly, more densely populated surface activity sites. However, how to control and improve the catalytic activity of the base metal catalysts is still a fundamental challenge in preparation, which needs to more detailed research for the interrelation between catalytic activity and preparation conditions.

To the best of our knowledge, there are few reports on the study of copper cobalt composite oxide catalysts prepared by co-precipitation method on CO oxidation at low temperature. Herein, we report the synthesis of copper cobalt composite oxide catalysts by this method. The catalytic activity and stability of the catalysts have been investigated. The interrelation between catalytic activity and the molar ratios of copper to cobalt, the volume of NaOH (2.0 mol/L), ageing time, calcination temperature, calcination time and the specific surface areas of the catalysts has been investigated in this paper.

EXPERIMENTAL

All chemicals obtained from Shanghai Chemical Reagent Ltd. Co. of China are analytical grade and used as received without further purification.

In a typical procedure, copper cobalt composite oxide catalysts were prepared by co-precipitation as follows: Aqueous solutions of CuSO₄·5H₂O (0.5 mol/L, 3 mL) and CoCl₂·6H₂O (0.5 mol/L, 15 mL) were pre-mixed. An aqueous solution of NaOH (2.0 mol/L, 12 mL) was added to the solution under vigorous stirring at ambient temperature. The precipitate was kept in the mother liquid for 6 h. Then the precipitate was filtered and washed with deionized water for several times. After being dried at 90 °C for 12 h in air, the samples were calcined at 150, 200, 300, 400 and 500 °C, respectively, for 3 h in air.

Characterization method: The phase purity and structure parameters of the samples were examined by power X-ray diffraction, using a Rigaku Dmax r-A X-ray diffractometer with graphite-monochromatized CuK_α

radiation ($\lambda = 1.5418 \text{ \AA}$), by a scanning rate of $0.05^\circ/\text{s}$ in the 2θ range from 10° to 70° , the operation voltage and current maintained at 40 kV and 40 mA. The structure of the samples was further examined with electron diffraction, transmission electron microscopy with a Hitachi model H-800 (Tokyo, Japan), the accelerating voltage of maintained at 200 kV. The X-ray photoelectron spectra (XPS) measurements were carried out on an ESCALAB MK II X-ray photoelectron spectrometer, using $\text{MgK}\alpha$ radiation as the exciting source. The XPS spectra were corrected by adjusting the C1s peak to a position of 284.6 eV. The thermogravimetry-differential thermal analysis (TG-DTA) of the sample was conducted on a Rigaku Standard Model thermal analyzer (in air atmosphere, flow rate: 90 mL min^{-1} ; heat rate: $10 \text{ }^\circ\text{C min}^{-1}$). The specific surface areas (S_{BET}) of the catalysts were calculated from a multipoint Braunauer-Emmett-Teller (BET) analysis of the nitrogen adsorption isotherms at 77 K recorded on an Omnisorp 100CX instrument. The catalytic activity and stability of the catalysts were evaluated on a small fixed-bed reactor operating under atmospheric pressure and an online GC using 100 mg sample of 40-80 meshes. The flow rate of the feed gas was 30 mL min^{-1} . The analysis of the effluent gas was tested with an online FuLi9790 model gas chromatograph with a Molecular Sieve 5 \AA column and a thermal conductivity detector (TCD). The catalysts were directly exposed to reaction gas containing 2.5 % (v/v) CO, 10 % (v/v) O_2 and 87.5 % (v/v) N_2 .

RESULTS AND DISCUSSION

Structure characterization: XRD patterns of copper cobalt composite oxide catalysts calcined at different temperature are shown in Fig. 1. Obviously, the weak peaks partly overshadowed by the background profiles indicated a poor degree of crystallization of the samples. The catalysts are amorphous when the calcination temperature is below $300 \text{ }^\circ\text{C}$ and the catalysts become more crystalline when the calcination temperature increases from 300 to $500 \text{ }^\circ\text{C}$. The crystallinity of the catalysts increased with the calcination temperature increasing.

The general morphology of the sample calcined at $200 \text{ }^\circ\text{C}$ was investigated by transmission electron microscopy (TEM) and shown in Fig. 2a. From Fig. 2a, it is can be seen that the most of the sample are nanoplates. The cluster of needles may come into being from the crinkle of the nanoplates. The thickness of the plates is filmy which may result in the large specific surface areas (S_{BET}) of the sample. The corresponding electron diffraction (Fig. 2b) shows that it is polycrystalline.

Fig. 3 depicts the typical TG-DTA curves of the sample calcined at $200 \text{ }^\circ\text{C}$. The sharp endothermic peak below $100 \text{ }^\circ\text{C}$ could be attributed to

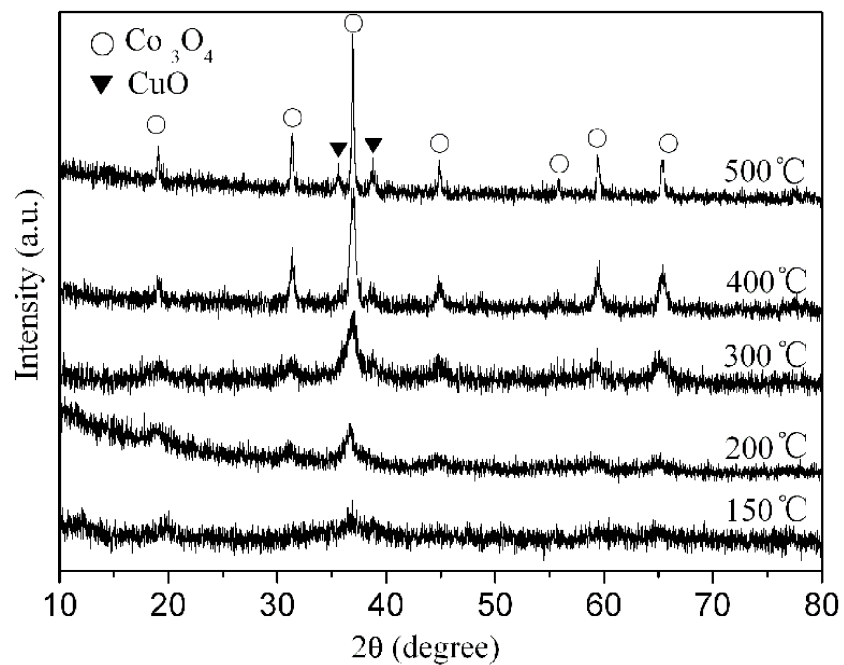


Fig. 1. XRD patterns of the catalysts calcined at different temperature

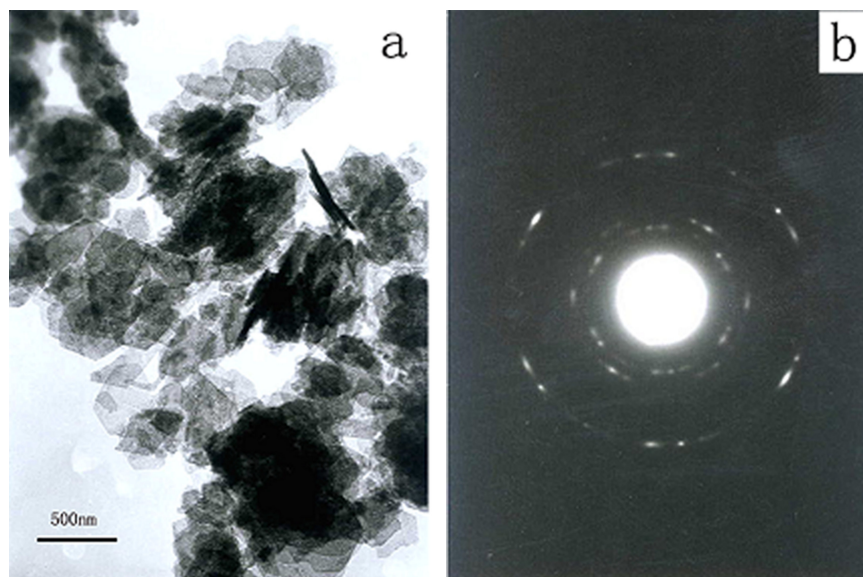


Fig. 2. TEM image (a) and ED pattern (b) of the catalyst calcined at 200 °C

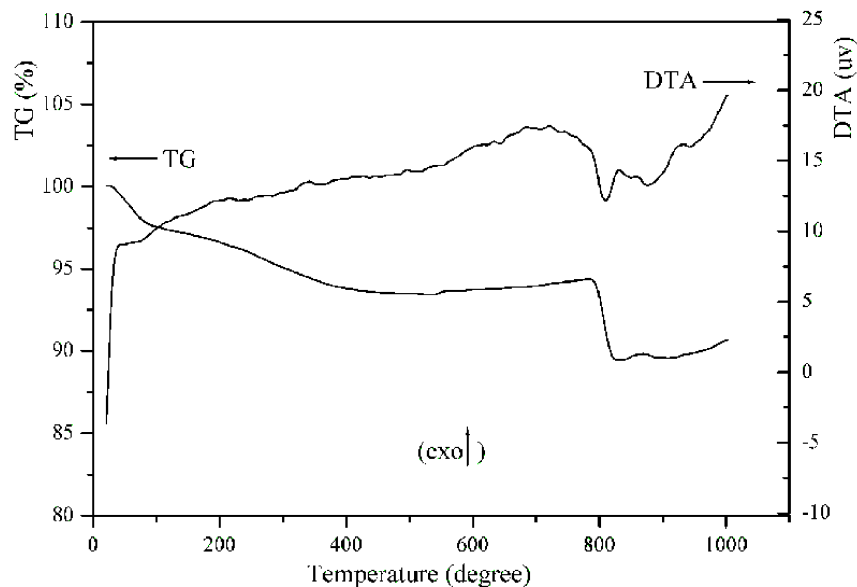


Fig. 3. TG-DTA curves of the catalyst calcined at 200 °C

the loss of surface absorbed water, which was confirmed by a dramatic weight loss 3 % wt in the TG curve over the corresponding temperature range. The weight loss 7 % wt between 100 and 500 °C on the TG curve could be explained that there is the removal of hydroxyl groups and crystallization process in this region. Correspondingly, there is no obvious endothermic peak on the DTA curve. Based on the TG-DTA results, it is safely concluded that the major phase composition of the catalyst calcined at 200 °C was copper cobalt composite oxide and hydroxide. On the basis of the above analysis, it is proposed that the active phase of the catalysts is metal oxides and hydroxides. As a matter of fact, hydroxide precursors sometimes could show higher activity than the oxides as confirmed by the reports from Haruta *et al.*³³⁻³⁶. Although the catalyst calcined at 200 °C is not pure CuO and Co₃O₄, it still exhibits the highest catalytic activity. This attributes to the related influential factors such as the molar ratios of copper to cobalt, the specific surface areas and the presence of the more active hydroxides and so forth.

Investigations by means of XPS were performed in order to illuminate the surface composition of the studied metal oxides, but also in order to acquire detailed information on the chemical state of the cations and anions. Further evidence for the quality and composition was obtained by X-ray photoelectron spectroscopy (XPS) of the fresh prepared catalysts calcined

at 200 °C. The spectra of the Cu 2p and Co 2p binding energies of the catalyst were shown in Fig. 4. In Fig. 4a, the peaks of Cu 2p_{3/2} and Cu 2p_{1/2} were centered at 933.8 and 953.4 eV, respectively. This suggests the presence of Cu(II) in the catalysts. The binding energy of Co 2p_{3/2} and Co 2p_{1/2} are about 779.2 and 794.3 eV, respectively (Fig. 4b). This suggests the presence of Co₃O₄ in the catalyst³⁷.

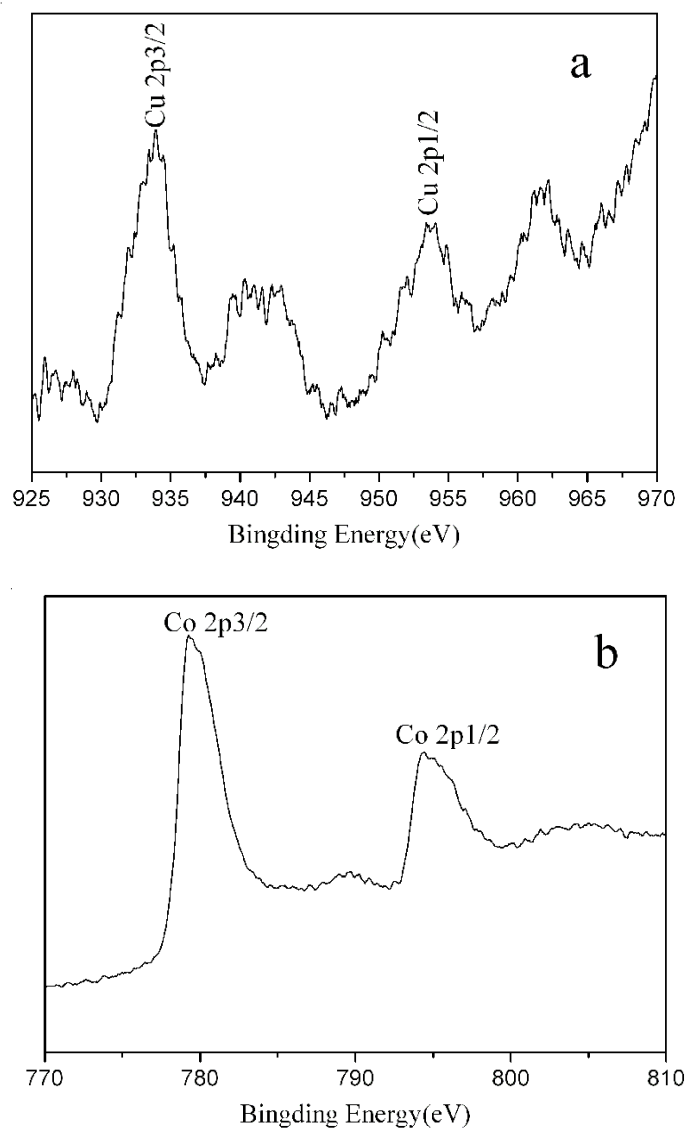


Fig. 4. XPS analysis of the catalyst calcined at 200 °C
(a) Cu spectrum (b) Co spectrum

Activity and stability tests of the catalysts: According to the coprecipitation method as above, the molar ratios of copper to cobalt, volume of NaOH (2 mol/L), ageing time, calcination temperature and calcination time was changed respectively while other factors were kept the same. The catalytic activity of the products was evaluated and the results were shown in Fig. 5. From Fig. 5 the optimal preparation conditions of the composite oxide catalysts can be fixed as follows: molar ratios of copper to cobalt 1:5, volume of NaOH (2 mol/L) 12 mL, ageing time 6 h, calcination temperature 200 °C and calcination time 3 h.

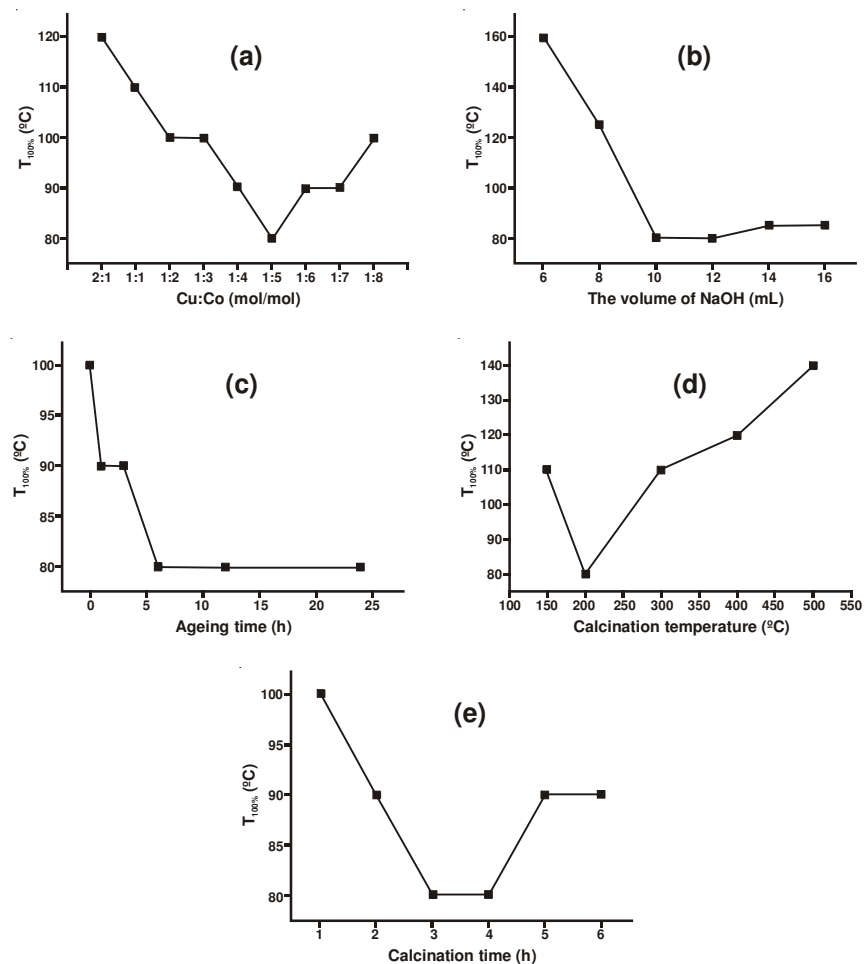


Fig. 5. The preparation conditions of the catalysts: (a) Cu:Co (mol/mol), (b) NaOH solution volume (mL), (c) ageing time (h), (d) calcination temperature (°C), (e) calcination time (h)

Among these influence factors, the molar ratios of copper to cobalt may have important effect on the catalytic activity of the catalysts. From Fig. 5a, the catalytic activity increased with increasing the molar ratios from 1:8 to 1:5 and decreased from 1:5 to 2:1. The catalyst with molar ratio of 1:5 exhibited highest catalytic activity on CO oxidation with lowest $T_{100\%}$. These results indicated that increasing the copper content in the catalysts can promote the catalytic activity of the catalysts to some extent, but it is not always true. These results may be from copper species having more chance to aggregation after their content attains a certain value. As Tang *et al.*¹⁶ suggest that the catalytic activity of the catalysts is strongly influenced by the dispersion of the copper species on the catalysts, it is proposed that the observed changes of the catalytic activity were probably due to the influence of different copper content in the catalysts, which results in the different dispersion of copper on the catalysts and probably changes the active sites on the surface of the catalysts and the catalytically active components of the catalysts³⁸. Therefore, the optimal molar ratio should be fixed at 1:5 to obtain the catalyst with high catalytic activity.

The catalytic activity and stability of the catalysts calcined at different temperature are investigated. The results are presented in Figs. 6 and 7. Fig. 6 shows that the catalysts calcined at 200 °C exhibited the highest catalytic activity on CO oxidation with CO total conversion at 80 °C. The catalytic activity of the catalysts increased with the reaction temperature increasing for all of the catalysts. The catalytic activity of the catalysts calcined at different temperature increased by increasing the calcination temperature from 150 to 200 °C and decreased from 200 to 500 °C. In Fig. 7, the reactor temperature was maintained at 70 °C, all of the catalysts showed an initial decrease in catalytic activity over first 40 min on line, but after this steady state period the catalytic activity was maintained over 400 min test period. The initial deactivation at the start of the catalyst evaluation may be result from the interaction between the reactants and the oxides, through which redox balance and stable surface composition were established in the initial stage. The steady state was attained after the initial stage and maintained over 400 min. On the basis of the above experiment results, it can be concluded that the catalytic activity and stability of the copper cobalt composite oxide catalysts on CO oxidation at low temperature is quite high.

For comparison, the individual CuO and Co₃O₄ samples were prepared through the same method and their catalytic activity on CO oxidation was evaluated in the same way. The specific surface areas (S_{BET}) and $T_{100\%}$ of the catalysts calcined at different temperature and individual CuO and Co₃O₄ samples are presented in Table-1. The $T_{100\%}$ is here defined as the temperature where the conversion of CO reaches 100 %. From Table-1, it can be seen

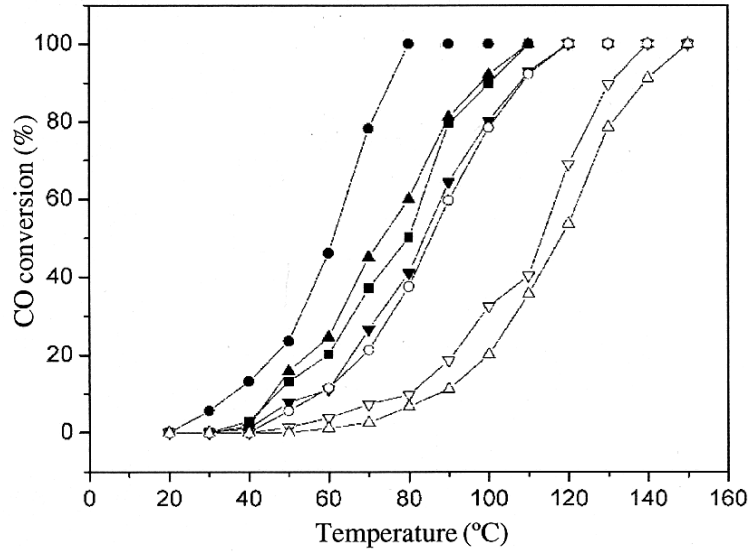


Fig. 6. Catalytic activity tests of the catalysts calcined at different temperature and the individual CuO and Co₃O₄ samples: (■) 150 °C, (●) 200 °C, (▲) 300 °C, (▼) 400 °C, (○) 500 °C, (Δ) CuO (▽) Co₃O₄

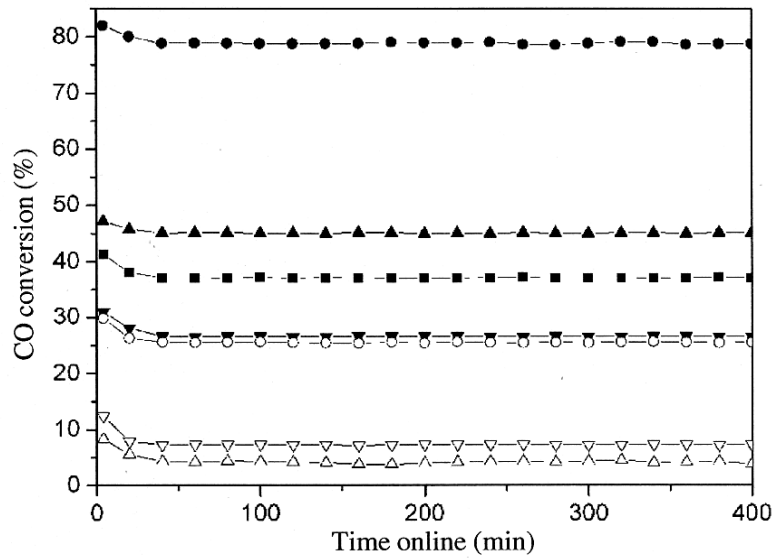


Fig. 7. Stability tests of the catalysts calcined at different temperature and the individual CuO and Co₃O₄ samples: (■) 150 °C, (●) 200 °C, (▲) 300 °C, (▼) 400 °C, (○) 500 °C, (Δ) CuO (▽) Co₃O₄

TABLE-1
 S_{BET} AND $T_{100\%}$ OF THE CATALYSTS CALCINED AT DIFFERENT
 TEMPERATURE AND THE INDIVIDUAL CuO AND Co_3O_4 SAMPLES

Catalysts	Caclination temperature (°C)	Surface area ($\text{m}^2 \text{g}^{-1}$)	$T_{100\%}$ (°C)
CuO	200	51.8	120
Co_3O_4	200	45.6	150
$\text{CuO}/\text{Co}_3\text{O}_4$	150	77.8	110
$\text{CuO}/\text{Co}_3\text{O}_4$	200	129.4	80
$\text{CuO}/\text{Co}_3\text{O}_4$	300	83.5	110
$\text{CuO}/\text{Co}_3\text{O}_4$	400	64.2	120
$\text{CuO}/\text{Co}_3\text{O}_4$	500	37.0	140

that the copper cobalt composite oxide catalysts exhibited obviously higher catalytic activity on CO oxidation than that of individual CuO and Co_3O_4 samples with lower $T_{100\%}$. This may be ascribed to a synergistic effect of the composite oxide caused by the interfacial metal-support interaction³⁹. The catalysts calcined at 200 °C exhibited the highest catalytic activity on CO oxidation with the lowest $T_{100\%}$ and had the largest S_{BET} . The S_{BET} of the catalysts increases slowly by increasing the calcination temperature from 150 to 200 °C and decreases rapidly from 200 to 500 °C. The observed modifications in the catalytic activity of the catalysts are result from the modifications of the S_{BET} of the catalysts, which are strongly dependent on their different calcination temperature. It can be concluded that the catalytic activity of the catalysts is strongly dependent on the S_{BET} and the calcination temperature.

Conclusion

In this work, we have successfully prepared the copper cobalt composite oxide catalysts by co-precipitation method. The products were characterized by X-ray diffraction, transmission electron microscopy, electron diffraction, X-ray photoelectron spectra, thermogravimetry-differential thermal analysis and nitrogen adsorption to determine the specific surface areas (S_{BET}). The catalytic activity and stability of the products were evaluated. The results indicate that the copper cobalt composite oxide catalysts exhibited obviously high catalytic activity on CO oxidation at low temperature. The copper cobalt composite oxide catalysts exhibited obviously higher catalytic activity on CO oxidation than that of individual CuO and Co_3O_4 samples. The interrelation between catalytic activity and the volume of NaOH (2 mol/L), ageing time, calcination temperature, calcination time, the molar ratios of copper to cobalt and the specific surface areas of the catalysts has been established. This preparation route is simple and low cost, which may offers

a potential applicability in many aspects, such as the technological potentiality applications for catalysts in place of three-way catalysts in automobiles exhaust control. This system is now worthy for further investigation.

REFERENCES

1. M. Kang, M.W. Song and C.H. Lee, *Appl. Catal. A*, **143**, 251 (2003).
2. Y.Z. Yuan, A.P. Kozlova, K. Asakura, H.L. Wan, K. Tsai and Y. Iwasawa, *J. Catal.*, **191**, 170 (1997).
3. S.D. Gardner, G.B. Hoflund and M.R. Davidson, *Langmuir*, **7**, 2140 (1991).
4. R.J.H. Grisel and B.E. Nieuwenhuys, *J. Catal.*, **48**, 199 (2001).
5. M. Date and M. Haruta, *J. Catal.*, **221**, 201 (2001).
6. N.A. Hodge, C.J. Kiely, R. Whyman, M.R.H. Siddiqui, G.J. Hutchings, Q.A. Pankhurst, F.E. Wagner, R.R. Rajaram and S.E. Golunski, *Catal. Today*, **72**, 133 (2002).
7. P. Bera and M.S. Hegde, *Catal. Lett.*, **79**, 75 (2002).
8. A. Martí'nez-Arias, J.M. Coronado, R. Catalun, J.C. Conesa and J. Soria, *J. Phys. Chem. B*, **102**, 4357 (1998).
9. M. Okumura, N. Masuyama, E. Konishi, S. Ichikawa and T. Akita, *J. Catal.*, **208**, 485 (2002).
10. W. Liu and M. Flytzani-Stephanopoulos, *J. Catal.*, **153**, 304 (1995).
11. W. Liu and M. Flytzani-Stephanopoulos, *J. Catal.*, **153**, 317 (1995).
12. T. Cheng, Z.Y. Fang, Q.X. Hu, K.D. Han, X.Z. Yang and Y.J. Zhang, *Catal. Commun.*, **8**, 1167 (2007).
13. T.J. Huang and D.H. Tsai, *Catal. Lett.*, **87**, 173 (2002).
14. W.P. Dow, Y.P. Wang and T.J. Huang, *J. Catal.*, **160**, 155 (1996).
15. W.P. Dow and T.J. Huang, *J. Catal.*, **160**, 171 (1996).
16. X.L. Tang, B.C. Zhang, Y. Li, Y.D. Xu, Q. Xin and W.J. Shen, *Catal. Today*, **93**, 191 (2004).
17. Y.J. Zhang, Q.X. Hu, B. Hu, Z.Y. Fang, Y.T. Qian and Z.D. Zhang, *Mater. Chem. Phys.*, **96**, 16 (2006).
18. P. Thormahlen, M. Skoglundh, E. Fridell and B. Andersson, *J. Catal.*, **188**, 300 (1999).
19. Y.J. Mergler, A.V. Aalst, J.V. Delft and B.E. Nieuwenhuys, *Appl. Catal. B*, **10**, 245 (1996).
20. Y.J. Mergler, J. Hoebink and B.E. Nieuwenhuys, *J. Catal.*, **167**, 305 (1997).
21. M. Meng, P.Y. Lin and Y.L. Fu, *Catal. Lett.*, **48**, 213 (1997).
22. L. Simonot, F. Garin and G. Maire, *Appl. Catal. B*, **11**, 167 (1997).
23. J. Jansson, A.E.C. Palmqvist, E. Fridell, M. Skoglundh, L. Osterlund, P. Thormahlen and V. Langer, *J. Catal.*, **211**, 387 (2002).
24. J. Jansson, *J. Catal.*, **194**, 55 (2000).
25. C.B. Wang, C.W. Tang, H.C. Tsai and S.H. Chien, *Catal. Lett.*, **107**, 223 (2006).
26. X.C. Zheng, S.H. Wu, S.P. Wang, S.R. Wang, S.M. Zhang and W.P. Huang, *Appl. Catal. A*, **283**, 217 (2005).
27. D.H. Tsai and T.J. Huang, *Appl. Catal. A*, **223**, 1 (2002).
28. D.M. Whittle, A.A. Mirzaei, J.S.J. Hargreaves, R.W. Joyner, C.J. Kiely, S.H. Taylor and G.J. Hutchings, *Phys. Chem. Chem. Phys.*, **4**, 5915 (2004).
29. S.H. Taylor, G.J. Hutchings and A.A. Mirzaei, *Chem. Commun.*, **15**, 1373 (1999).
30. T.H. Rogers, C.S. Piggot, W.H. Bahlke and J.M. Jennings, *J. Am. Chem. Soc.*, **43**, 1973 (1921).
31. H.A. Jones and H.S. Taylor, *J. Phys. Chem.*, **27**, 623 (1923).
32. J.W. Saalfrank and W.F. Maier, *Chimie*, **7**, 483 (2004).
33. M. Date and M. Haruta, *J. Catal.*, **201**, 221 (2001).

34. B.S. Uphade, Y. Yamada, T. Akita, T. Nakamura and M. Haruta, *Appl. Catal. A*, **215**, 137 (2001).
35. T. Akita, M. Okumura, K. Tanaka, M. Kohyama and M. Haruta, *Catal. Today*, **117**, 62 (2006).
36. G.J. Hutchings and M. Haruta, *Appl. Catal. A*, **291**, 2 (2006).
37. C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G.E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, New York, CT (1979).
38. I.W. Onuchkwu, *J. Chem. Soc. Faraday Trans.*, **180**, 1447 (1984).
39. R. Burch and A.R. Flambard, *J. Catal.*, **78**, 389 (1982).

(Received: 24 September 2007;

Accepted: 10 March 2008)

AJC-6447