Impregnation method prepared Cu-Co-Ce-O catalysts and their activities for low-temperature carbon monoxide oxidation

Yan Wang[a,b], Jie Kong[b], Zhaoli Yan[c], Zhanying Zhang[c*], Jianliang Cao[c*], Guang Sun[c], Hari Bala[c]

[a]State Key Laboratory Cultivation Base for Gas Geology and Gas Control (Henan Polytechnic University), Jiaozuo 454003, China

[b]Institute of Safety Science and Engineering, Henan Polytechnic University, Jiaozuo 454003, China

[c]Institute of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454003, China

Email addresses: zhangzy@hpu.edu.cn (Z.Y.Zhang), caojianliang@gmail.com (J.L. Cao)

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Abstract. The support CeO_2 was prepared by thermal decomposition method, and the Cu-Co-Ce-O catalysts were synthesized via impregnation method. The prepared catalysts were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) techniques, and their catalytic properties for low-temperature CO oxidation were evaluated by using a microreactor-GC system. The results showed that the Co/Ce atomic ratio has great effect on the activities of catalysts, and the catalyst with Co/Ce = 1 has the highest catalytic activity for CO total oxidation at 90 ^{o}C.

Introduction

Carbon monoxide, which is emitted from many industrial and transportation activities, is one of the major air pollutants that are harmful to human health and the environment. In order to control the toxic emission, catalytic oxidation of CO is an efficient way. Recently, lots of catalysts have been investigated, in which precious metal catalysts such as Pd/SnO_2, Au/MnO_x, Au/α-Fe_2O_3, Pt/SnO_2 and Au/SnO_2 have been demonstrated to be very effective [1-3]. However, their extensive adoption is discouraged by their high cost and limited availability. Much attention has thus recently been paid to base metal as catalysts, for both their excellent performances in CO oxidation and low cost.

Cerium dioxide is of interest for its applications such as three-way catalysts for automotive exhaust gas treatment. CeO_2 supported precious metal and CuO catalysts have been used for carbon monoxide oxidation [4-6]. Recently, Ce-containing mixed oxides, such as CeO_2-ZrO_2, CeO_2-CoO, and CeO_2-TiO_2 have been proposed as oxidation catalysts [7-10]. However, the doping of ceria with other elements did not always enhance the activity of CuO/CeO_2 catalysts in catalytic oxidation. Wu et al. [10] prepared $CuO/Ce_{1-x}Ti_xO_2$ by a sol-gel impregnation method and studied its catalytic activity for the preferential oxidation of CO in H_2-rich streams. The catalyst with a composition of $CuO/Ce_{0.8}Ti_{0.2}O_2$ exhibited the highest activity. Our previous studies [7] found that incorporating zirconium into CeO_2 could improve the oxygen storage capacity, redox properties and thermal resistance of the resulting mixed oxides. The mesoporous $CuO/Ce_{0.8}Zr_{0.2}O_2$ nanocatalysts exhibited the highest catalytic activity for low temperature CO oxidation (total oxidation of CO at 90 ^{o}C). In recent years, it has been found that the incorporating of cobalt can improve CO oxidation activities of Pt/SiO_2 and Au/SiO_2 catalysts [11, 12]. In the previous work [9], we have synthesized Cu-Co-Ce-O catalysts by the co-precipitation method and found that which show high catalytic activities for low-temperature CO oxidation for CO total oxidation at 75 ^{o}C. Thus, it seems reasonable to devolop a Ceria-based catalyst doped with copper and cobalt, which would have either high activity for low-temperature CO oxidation or high thermal stability.

In this paper, we report the thermal decomposition method prepared of CeO_2 support, and the impregnation method prepared of Cu-Co-Ce-O catalysts. The low-temperature carbon monoxide oxidation activities of the as-prepared catalysts were systematically investigated. The analysis results

presented that when $x = 0.4, 0.5, 0.6, 0.8$, the cubic spinel structure typical of $Cu_{0.76}Co_{2.24}O_4$ was formation. When $x = 0.6, 0.8$, CuO was partially formation $Cu_{0.76}Co_{2.24}O_4$ in these two samples, some CuO was dispersed on the surface of CeO_2. The catalytic activities measurement results showed that the as-prepared Cu-Co-Ce-O catalysts presented high activities for low-temperature CO oxidation.

Experimental Section

Preparation of CeO$_2$ support. The support CeO_2 was prepared by thermal decomposition method. The precursor $Ce(NO_3)_3 \cdot 6H_2O$ was put in a muffle furnace and calcined at 500 ^oC for 4 h for the formation of CeO_2 nanoparticles.

Preparation of Cu-Co-Ce-O catalysts. The Cu-Co-Ce-O catalysts (abbreviated as $Cu_{0.1}Co_xCe_{1-x}$) were synthesized by impregnation method. The calculated amounts of $Cu(NO_3)_2 \cdot 3H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in distilled water, then stirred about 20 min and the caculated amount of as-prepared CeO_2 was added in the solution. Further vigorous stirring 5h under room temperature, evaporation at 50 ^oC, oven dried at 80 ^oC overnight, then calcined at 400 ^oC for 4 h in air in a muffle furnace. The $Cu_{0.1}Co_xCe_{1-x}$ ($x = 0.2, 0.4, 0.5, 0.6, 0.8$) catalysts were obtained.

Catalyst Characterization. X-ray diffraction (XRD) analysis was performed on a Rigaku D/max-2500 diffractometer, with Cu Kα radiation at 40 kV and 100 mA in a scanning range of $3 - 80^o$ (2θ). The diffraction peaks of the crystalline phase were compared with those of standard compounds reported in the JCPDS (Joint Committee on Powder Diffraction Standards) Date File. The Fourier transform infrared spectra (FT-IR) were recorded with a model MAGNA-560 Infrared Fourier Transform Spectrometer (Nicolet) in the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} .One milligram of each powder sample was diluted with 100 mg of potassium bromide (KBr) powder.

Catalytic oxidation of CO. Catalytic activity tests of the prepared $CuO/Ce_xSn_{1-x}O_2$ catlysts were performed in a continuous-flow fixed-bed microreactor. A stainless steel tube with an inner diameter of 7 mm was chosen as reactor tube. About 200 mg of catalyst power was placed into the tube. The reaction gas mixture consisting of 10 vol% CO balanced with air was passed through the catalyst bed at a total flow rate of 36.6 mL/min. A typical weight hourly space velocity (WHSV) was 11000 mL/h/g. After 30 min reaction, the effluent gases were analyzed online with a GC-900A gas chromatograph equipped with a TCD. The activity is expressed as the conversion of CO.
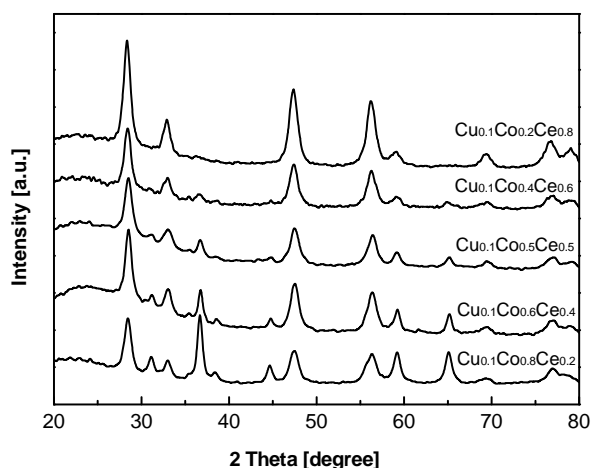
Results and Discussion

Fig.1 XRD patterns of 400 ^oC-calcined $Cu_{0.1}Co_xCe_{1-x}$ catalysts

The typical diffraction pattern of the as-prepared Cu-Co-Ce-O ($Cu_{0.1}Co_xCe_{1-x}$) catalysts with varying Co/Ce atomic ratio is shown in Fig. 1. It can be seen clearly from Fig. 1 that the cubic, fluorite type of CeO_2 (compared with JCPDS Date File # 34-394) are clearly observed for all the catalysts.

When x = 0.4, 0.5, 0.6, 0.8, there are four main reflections at 2θ = 31.1, 36.7, 44.7 and 65.1º, corresponding to the cubic spinel structure typical of $Cu_{0.76}Co_{2.24}O_4$ (compared with JCPDS Date File # 36-1189). When x = 0.6, 0.8, there are characteristic diffraction peaks appeared at 2θ = 35.4, 38.6º. This indicates that CuO was partially formation $Cu_{0.76}Co_{2.24}O_4$ in these two samples, some CuO was dispersed on the surface of CeO_2.
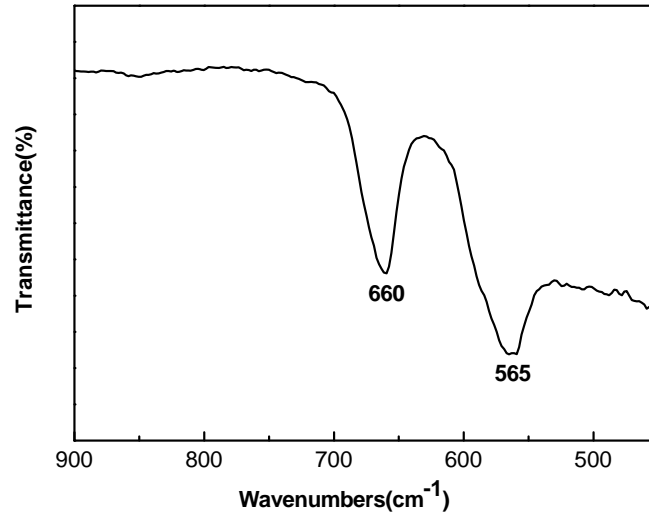
Fig. 2 FT-IR spectra of 400 ºC-calcined $Cu_{0.1}Co_{0.5}Ce_{0.5}$ catalyst

Fig. 2 shows the FT-IR spectra of $Cu_{0.1}Co_{0.5}Ce_5$ catalyst. There are two obvious bands at about 660 cm^{-1}（v_1）and 565 cm^{-1} (v_2), which can be attributed to the stretching vibration of the Co-O bond. The v_1 band is attributed to OB_3 vibration in the spinel lattice, where B denotes the Co^{3+} in octahedral hole. While, the v_2 band is characteristic of ABO_3 vibration in the spinel lattice (A denotes the Co^{2+} in tetrahedral hole).
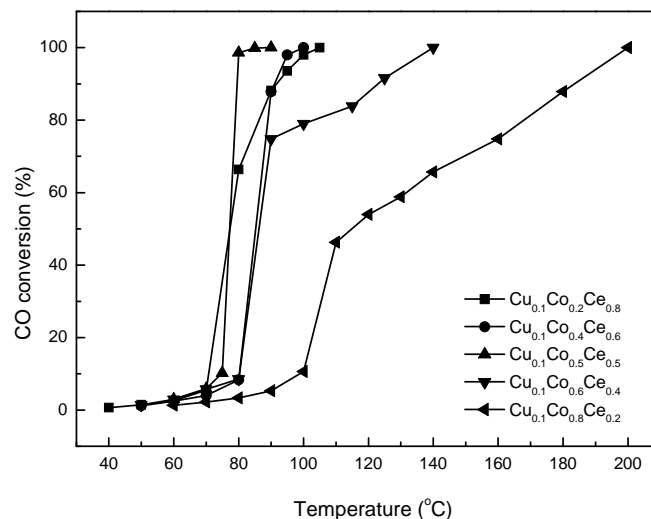

Fig. 3 Catalytic activities of $Cu_{0.1}Co_xCe_{1-x}$ catalysts with different Co/Ce atomic ratios for CO oxidation

Fig. 3 shows the effect of Co/Ce ratio on the low-temperature CO oxidation activity of $Cu_{0.1}Co_xCe_{1-x}$ catalysts. The results show a similar behavior that the CO oxidation activity of all the $Cu_{0.1}Co_xCe_{1-x}$ samples increased with the increase of the catalytic reaction temperature measured in the catalyst bed. It can be observed from Fig. 3 that all the $Cu_{0.1}Co_xCe_{1-x}$ catalysts show much higher catalytic activity. It can be also seen that the Co/Ce ratio have larger effect on catalytic activity of the

as-prepared catalysts. When Co/Ce ratio = 1, the catalyst exhibits the highest catalytic activity on CO oxidation with CO total conversion at 90 ºC. The Co/Ce atomic ratio of less than 1 catalyst show higher activity than that of the Co/Ce atomic ratio catalyst.

Conclusions

In summary, we have presented a facile route to prepare the CeO_2 and Cu-Co-Ce-O catalysts by a impregnation method. The XRD analysis results presented that when x = 0.4, 0.5, 0.6, 0.8, the cubic spinel structure typical of $Cu_{0.76}Co_{2.24}O_4$ was formation. When x = 0.6, 0.8, CuO was partially formation $Cu_{0.76}Co_{2.24}O_4$ in these two samples, some CuO was dispersed on the surface of CeO_2. Due to synergetic effects, the incorporation of Co into CeO_2 in the Cu-Co-Ce-O catalysts promoted the CO oxidation activity and the $Cu_{0.1}Co_{0.5}Ce_5$ catalyst was the most active for CO total oxidation at 90 ºC. And, we will further study the effect of calcination temoerature and CuO content on the activity of Cu-Co-Ce-O catalysts for low-temperature CO oxidaiton.

Acknowledgements

References

[1] D.R. Schryer, B.T. Upchurch, B.D. Sidney, K.G. Brown, G.B. Hoflund and R.K. Herz: J. Catal. 130 (1991), p. 314 .

[2] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and B. Delmon: J. Catal. 144 (1993), p. 175

[3] S.R. Wang, J. Huang, Y.Q. Zhao, S.P. Wang, X.Y. Wang, T.Y. Zhang, et al.: J. Mol. Catal. A. 259 (2006), p.245

[4] X.C. Zheng, S.H. Wu, S.P. Wang, S.R. Wang, S.M. Zhang, W.P. Huang: Appl. Catal. A. 283 (2005), P.217

[5] C.R. Jung, J. Han, S.W. Nam, T.H. Lim, S.S. Hong, H.I. Lee: Catal Today 93-95 (2004), P.183

[6] X.Y. Wang, S.P. Wang, S.R. Wang, Y.Q. Zhao, J. Huang, S.M. Zhang, W.P. Huang and S. H. Wu: Catal. Lett. 112 (2006), p.115

[7] J.L. Cao, Y. Wang, T.Y. Zhang, S.H. Wu and Z.Y. Yuan: Appl. Catal. B. 78 (2008), p. 120

[8] J. Huang, S.R. Wang, X.Z. Guo, D. Wang, B.L. Zhu and S.H. Wu: Catal Commun. 9 (2008), p. 2131

[9] Y. Su, S.P. Wang, T.Y. Zhang, S.R. Wang, B.L. Zhu, J.L. Cao, Z.Y. Yuan, S.M. Zhang, W.P. Huang and S.H. Wu: Catal. Lett. 124 (2008), p. 405

[10] Z.W. Wu, H.Q. Zhu, Z.F. Qin, H. Wang, L.C. Huang and J.G. Wang: Appl. Catal. B. 98 (2010), p. 204

[11] Y.J. Mergeler, A.van. Aalst, J.van. Delft, and B.E. Nieuwenhuys: Appl. Catal. B. 10 (1996), p. 245

[12] K. Qian, W.X. Huang, Z.Q Jiang, and H.X Sun: J. Catal. 248 (2007), p. 137