[Article ID] 1003- 6326(2002)02- 0317- 04

Synthesis and catalytic property of Cu-Mn-Ce/ γ-Al_2O_3 complex oxide①

HUANG Ke-long(黄可龙), WANG Hong-xia(王红霞), LIU Su-qin(刘素琴), GUI Ke(桂 客)
(College of Chemical and Chemistry Engineering, Central South University, Changsha 410083, China)

[Abstract] A new type of catalytic material for purification of automobile exhaust, Cu-Mn-Ce-O/ γ-Al_2O_3, has been studied. The factors affecting its catalytic activity, such as calcination temperature and the period of calcinations and so on have been investigated. Its catalytic activity after SO_2-poisoning was determined in a fixed-bed reactor by exposing the sample to the atmosphere of 160 mL/ min SO_2/ air. The study reveals that the catalyst has shown high catalytic activities for the conversion of NH_3 oxidation by NO after sulfate. The conversion of NO reduction over the sulfated catalyst is somewhat higher than that over the fresh catalyst except that the optimum temperature has increased about 100 ℃. Also at the optimum process for the experiment, the selective catalytic oxidation of CO by NO is over 76% and the conversion of NO reduction is over 80% by NH_3.

[Key words] purifying material; automobile exhaust; catalytic activity; bimetallic oxide catalyst; resistance to SO_2-poisoning

[CLC number] O 643.36 [Document code] A

1 INTRODUCTION

The increasingly stringent government regulations on the emission level of exhaust from transportation vehicles resulted in the recent intense research in the area of purifying catalysts. This is particularly for the reduction of NO to N_2 with hydrocarbons and the oxidation of CO to CO_2 with NO. The highly developed three-way-catalyst are made of precious metal Pt, Pd and Rh, the limited natural resources of which led to high price[1~3]. On the other hand, traditional catalyst doesn't take effect efficiently in the presence of high concentration of SO_2 because of the formation of sulfate[4]. So it is necessary to investigate new catalysts for practical use with low-cost, high resisting to SO_2-poisoning. In this respect, great efforts have been made by different authors[5~7]. In this article, a new type of purifying catalysts Cu-Mn-Ce/ γ-Al_2O_3 for automobile exhaust has synthesized by impregnation method with its properties characterized through XRD and BET techniques, and its performance was tested with CO-NO and NH_3-NO as probe molecules and its catalytic activity after sulfated by SO_2 is also discussed.

2 EXPERIMENTAL

2.1 Preparation of materials

The Ceria-Aluminum support was prepared by grafting $Ce(NO_3)_2$ on an aluminum support and calcined at 773 K. Then this support was impregnated with aqueous solutions of $Cu(NO_3)_2$ and $Mn(NO_3)_2$ in order to prepare bimetallic catalysts with a global metal content between 10% ~ 17%. The impregnated support was dried overnight in air at 150 ℃ and then treated at a certain temperature for 2 h. The sulfated catalyst of Cu-Mn-Ce/ γ-Al_2O_3 was tested in a fixed-bed flow reactor under 3.0% SO_2/ air flow rate of 160 mL/ min for 5.0 h at 500 ℃ to produce bulk sulfation.

2.2 Catalytic testing

The catalytic testing was carried out in a fixed-bed reactor as shown in Fig. 1 in a flow of 1% to 3% O_2, 0.1 NO% and 3% CO, or simulated gas of 0.08% NO, 3% O_2 and 0.8% NH_3 with the rest being He. The total flow rate of 160 mL/ min and 5 mL of catalyst was used, and the corresponding space velocity was $9.6\times10^4 h^{-1}$. The gases were analyzed by gas chromatography 4100 with the data treated by data station, and CO conversions was determined by the CO_2 produced and NO conversion was measured by the N_2 produced.

3 RESULTS AND DISCUSSION

3.1 Effect of calcination temperature on catalytic activity

The catalytic activity of Cu-Mn-Ce/ γ-Al_2O_3 for the oxidation conversion of CO by NO was investigated in a flow reactor as described above. The catalysts were pretreated in H_2 atmosphere at 200 ℃ for 2 h before testing its performance. A typical reaction profile as a function of calcination temperature was reported for the catalyst in Fig. 2.

Fig. 2 depicts the influence of calcination tempe-

① [Received date] 2001- 07- 27; [Accepted date] 2001- 09- 17

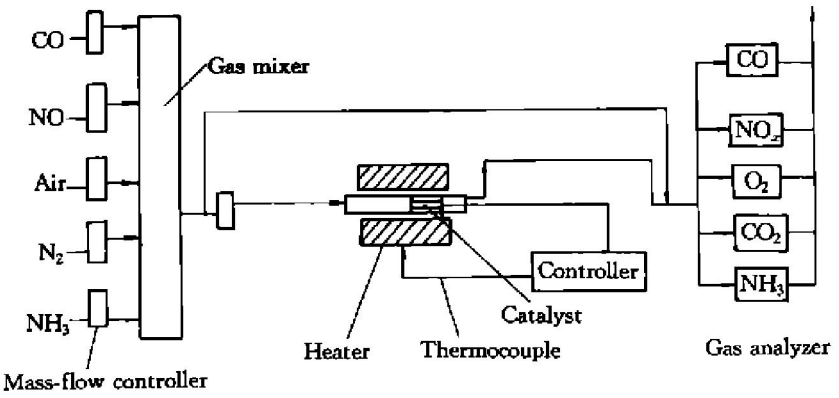

Fig. 1 Schematic diagram of a quartz tubular fixed-bed reactor

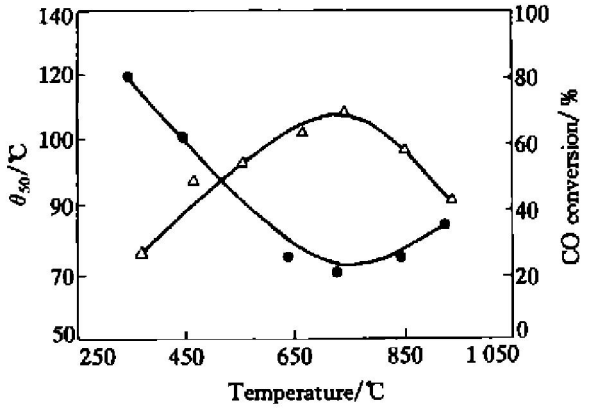

Fig. 2 Relationship between activity and calcination temperature
θ_{50} —Temperature for 50% CO conversion;
△ —Conversion of CO at 100 ℃;
● —Effect of calcination temperature on θ_{CO}

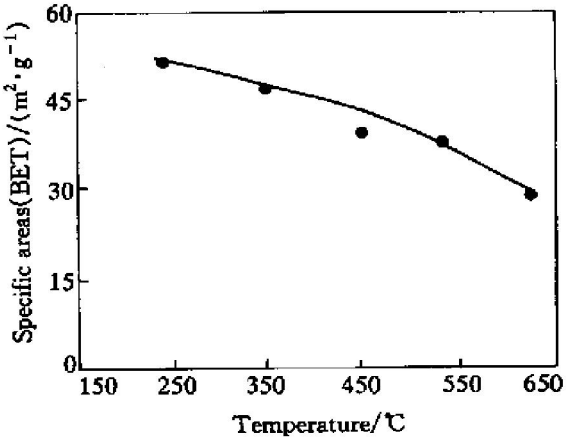

Fig. 3 Effect of calcination temperature on specific areas of catalyst

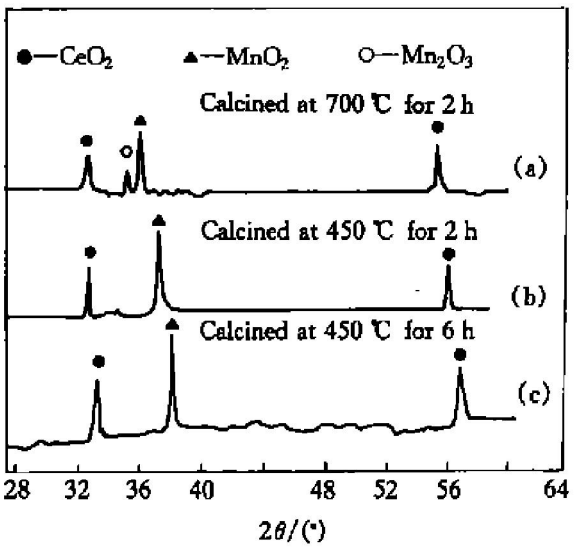

Fig. 4 XRD of catalysts
(a) —Catalyst calcined at 700 ℃ for 2 h;
(b) —Catalyst calcined at 450 ℃ for 2 h;
(c) —Catalyst calcined at 450 ℃ for 6 h

rature on the catalytic activity of Cu-Mn-Ce/ γ-Al_2O_3 for the conversion of CO, oxidated by NO. Notes to be paid is that θ_{50} represents the reaction temperature of the samples for the 50% conversion of CO. As can be seen apparently from these data that calcination temperature exerts a pronounced effect on the activity. The conversion of CO initially increases with the increase of calcination temperature before it amounts to 700 ℃, then decreased with further increase in the calcination of temperature at reaction temperature of 100 ℃, and accordingly θ_{50} is decreased significantly at first with the increasing calcination temperature before it reached 700 ℃ and then increased with further increase of calcination temperature. In order to explain this results, we further studied the effect of calcination temperature on the specific areas (BET) of the samples, which is illustrated in Fig. 3 and the XRD of the catalysts calcined at 450 ℃ and 700 ℃ respectively for 2 h which is shown in Fig. 4(a) and 4 (b). As can be seen in Fig. 3, the higher calcinations temperature of the samples is, the less BET of Cu-Mn-Ce/ γ-Al_2O_3 is, which will lead to lower activity of the catalysts.

XRD reveals the variation of structure of the catalyst, so we studied the structure of the catalysts by changing the calcination temperature and found there is a typical peak of Mn_2O_3 in the sample calcined at 700 ℃ which didn't appear in another sample cal-

cined at 450 ℃, therefore we can reach a conclusion that the appearance of Mn_2O_3 at high calcinations temperature resulted in the increased activity of the catalyst. LU et al[7] reported that MnO has high catalytic activity to the conversion of NO by oxidation and Karlsson et al[8] also studied the catalytic activity of a series of such transitional elements as Cu, Mn, Co, Fe for the conversion of NO by oxidation and found the order of their activity is CoO > MnO_2 > Fe_2O_3 > CuO. So we can say the new phase Mn_2O_3 is the transitional state of MnO and MnO_2, the catalytic activity of which is higher than that of MnO and MnO_2. Moreover, at high calcination temperature, the interaction of Cu and Ce occurs, which leads to the formation of high catalytic activity structure Cu-Ce-O, including fluorite-type structure of CeO_2 and monoclinic structure of CuO, however when the temperature is above 700 ℃, the doped CuO is separated out of the lattice of CeO_2, which results in the decrease of oxygen vacancies and the catalytic activity.

3.2 Influence of calcination time

Fig. 5 demonstrates the influence of the time of calcinations at a certain temperature on the catalytic activity of Cu-Mn-Ce/ γ-Al_2O_3. As can be seen from these data, the oxidation conversion of CO by NO reaches maximum when calcination time is about 2.5 h, and the CO conversion then decreases with the time prolongation. Meanwhile the diagram of the XRD of the catalyst calcined at 450 ℃ for 2 h and 6 h respectively, though 450 ℃ is not the optimum one (Figs. 4(b) and (c)), is alike which reveals the chemical structure of the sample is alike too, but there is sintering on the surface of the sample calcined for 6h, which may cause the decrease of the catalyst activity.

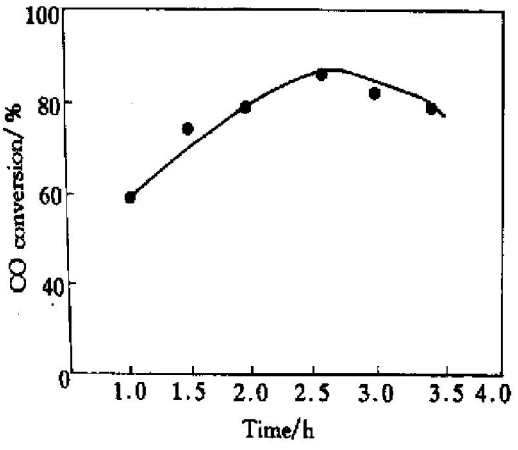

Fig. 5 Influence of calcination time at certain temperature on activity of the catalyst

3.3 Resisting to SO_2 poisoning

3.3.1 Effect of reaction temperature on conversion of NO

Fig. 6 illustrates clearly the effect of the reaction temperature on NO conversion over the fresh and bulk sulfated catalysts. It's apparently that the reaction temperature at which NO conversion exhibits the maximum values over the bulk sulfated Cu-Mn-Ce-O/ γ-Al_2O_3 catalyst was about 450 ℃, which is about 100 ℃ higher than that over the fresh catalyst. The optimum temperature shifting to higher temperature over the bulk sulfated catalyst could be related to adsorption and oxidation of NH_3 on the catalyst. The decrease of the reduction conversion of NO above the optimum temperature may be related with the following two reactions[10]:

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O \quad (1)$$

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O \quad (2)$$

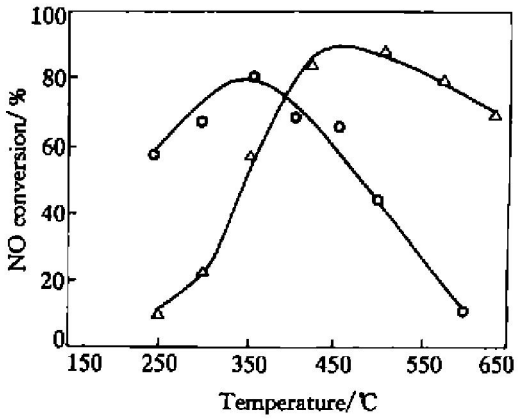

Fig. 6 Effect of reaction temperature on NO conversion over fresh and bulk sulfated catalysts
○—Fresh catalyst; △—Sulfated catalyst

The increase of the conversion of NH_3 oxidation by O_2 in reaction (1) causes a decrease on surface ammonia with NO for the reaction (2). Furthermore, we find maximum NO conversion on the bulk sulfated catalyst is also a little higher than that on the fresh catalyst. The enhanced activity of the bulk sulfated catalyst compared to that of the fresh catalyst may be due to an increase of the superacidity and the Brønst acidity that are caused by a surface ion of SO_4^{2-} on the catalyst[11,12], and we find the specific areas of the bulk catalysts are less than that of the fresh catalyst, and the deeper the degree of the sulfation is, the less the BET is, which will cause the decrease of the catalytic activity of Cu-Mn-Ce-O/ γ-Al_2O_3 catalyst.

3.3.2 Effect of reaction temperature on oxidation conversion of NH_3

In the system of the reaction of NO-NH_3, ammonium is mainly oxidized by reaction (1) above and partly by following reaction

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O \quad (3)$$

The effect of reaction temperature on NH_3 oxidation over the fresh and the bulk sulfated Cu-Mn-Ce-O/ γ-Al_2O_3 is shown in Fig. 7. As can be seen, oxida-

tion of NH_3 over the bulk sulfated catalyst starts to proceed at higher temperature. The temperature at which the conversion of NH_3 oxidation reaches 80% is 350 ℃ for the fresh catalyst and 450 ℃ for the bulk sulfated catalyst because of the difference in the surface compound with or without sulfate species on the catalyst. NH_3 over the bulk sulfated catalyst may not be oxidized by oxygen but adsorbed on sulfate surface $Al_2(SO_4)_3$, $CuSO_4$ and $MnSO_4$ of the catalyst to produce ammonium sulfate blow 300 ℃. $(NH_4)_2SO_4$ starts to be decomposed to produce SO_2 above 350 ℃, and thereafter NH_3 is oxidized to N_2 and a small amount of NO.

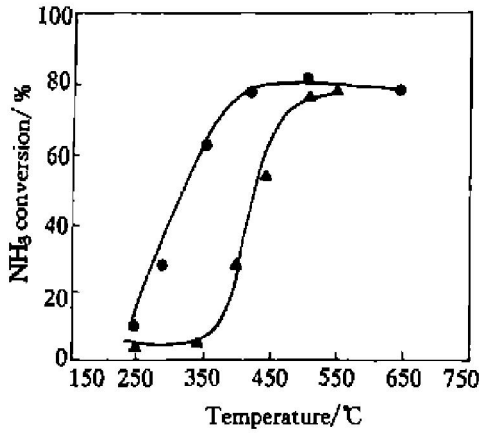

Fig. 7 Effect of reaction temperature on NH_3 conversion over fresh and sulfated catalysts
● —Fresh catalyst; ▲ —Sulfated catalyst

4 CONCLUTIONS

The bimetallic Cu-Mn-Ce/ γ-Al_2O_3 catalyst was prepared by grafting $Ce(NO_3)_2$ on an aluminum support and calcined at 773 K. Then this support was impregnated with aqueous solutions of $Cu(NO_3)_2$ and $Mn(NO_3)_2$, and dried and calcined in air at certain temperature. The factors affecting its catalytic activity in the system of NO-CO reaction and its activity for the oxidation conversion of NH_3 by NO after sulfated in the atmosphere of SO_2 in a fixed-bed reactor have been investigated.

The specific areas of the sample decreases with the increase in calcination temperature, while the catalytic activity of the sample increases with the increase in calcination temperature before it reaches 700 ℃ for the reaction of CO oxidation by NO.

The catalytic activity amounts to maximum at the calcinations temperature about 700 ℃ for 2.5 h for the system NO-CO, and sintering is found on the surface of the sample with prolonged calcinations, which may decrease the catalyst activity.

The optimum reaction temperature for NO reduction by NH_3 over the sulfated sample is about 450 ℃, which is 100 ℃ higher than that over the fresh catalyst. Also, NO conversion over the sulfated catalyst is somewhat higher than that over the fresh catalyst.

ACKNOWLEDGMENT

The research described in this article has been funded by the Science Committee of Hunan Province under assistance agreement [2000] 139, 1007-2 to the college of Chemical and Chemistry Engineering, Central South University.

[REFERENCES]

[1] Holmgren A, Andersson B. Oxygen storage dynamics in Pt/CeO_2 catalysts [J]. J Catal, 1998, 178: 14.
[2] Granger P, Lecomte J J, Dathy C. Kinetics of the CO+NO reduction over rhodium and platinum-rhodium on alumina [J]. J Catal, 1998, 175: 194.
[3] Rogemond E, Essayem N, Frety R. Characterization of model three-way catalysts [J]. J Catal, 1999, 186: 414.
[4] Xu C B, Wu S L. Experimental study on purification of NO_x in automobile exhaust using a new type of complex metal-oxide catalyst [J]. Chinese. Environmental Science, 1998, 19(3): .
[5] Kung M C, Park D W, Kim D W. Lean NO_x catalysis over Sn/ γ-Al_2O_3 catalysts [J]. J Catal, 1999, 181: 1-5.
[6] Fernandez-Garcia M, Martinet-Avias A. Behavior of palladium-copper catalysts for CO and NO elimination [J]. J Catal, 2000, 190: 387.
[7] LU Guan-zhong, WANG Xing-yi. Role of ceria in non-precious metal oxide catalysts (V) [J]. Chemical Journal of Chinese University, 1994, 6(15): 895.
[8] Lu W Z, Zhao X G, Wang H. Catalytic oxidation of NO [J]. Chin J Catal, 2000, 21(5): 423.
[9] Karlsson H T, Roseberg H S. Flue gas denitrification: selective catalytic oxidation of nitric oxide to nitrous oxide [J]. Ind Eng Chem Proc Des Dev, 1984, 23(4): 808.
[10] Centi G, Passarini N, Perathoner S. Combined $DeSO_x$/$DeNO_x$ reactiona on a copper on aluminum sorbent-catalyst. 3. $DeNO_x$ behavior as a Function of the surface coverage sulfated species [J]. Ind Eng Chem Res, 1992, 31: 1963.
[11] Kiel J H A, Edelaar A C S, Prins W. Performance of silica-supported copper oxide sorbents for SO_x/NO_x removal from flue gas. 2. selective catalytic reduction of nitric oxide by ammonia [J]. Appl Catal, 1992, 1: 41.
[12] Chen J P, Yang R T. Selective catalytic reduction of NO with NH_3 on SO_4^{2-}/TiO_2 superacid catalyst [J]. J Catal, 1993, 139: 277.

(Edited by ZHU Zhong-guo)