



## Catalytic reduction of nitric oxide with carbon monoxide on copper-cobalt oxides supported on nano-titanium dioxide

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### Abstract

A series of copper-cobalt oxides supported on nano-titanium dioxide were prepared for the reduction of nitric oxide with carbon monoxide and characterized using techniques such as XRD, BET and TPR. Catalyst  $\text{CuCoO}_x/\text{TiO}_2$  with Cu/Co molar ratio of 1/2, Cu-Co total loading of 30% at the calcination temperature of 350°C formed  $\text{CuCo}_2\text{O}_4$  spinel and had the highest activity. NO conversion reached 98.9% at 200°C. Mechanism of the reduction was also investigated,  $\text{N}_2\text{O}$  was mainly yielded below 100°C, while  $\text{N}_2$  was produced instead at higher temperature.  $\text{O}_2$  was supposed to accelerate the reaction between  $\text{NO}_x$  and CO for its oxidation of NO to give more easily reduced  $\text{NO}_2$ , but the oxidation of CO by  $\text{O}_2$  to  $\text{CO}_2$  decreased the speed of the reaction greatly. Either  $\text{SO}_2$  or  $\text{H}_2\text{O}$  had no adverse impact on the activity of NO reduction; however, in the presence of both  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , the catalyst deactivated quickly.

**Key words:**  $\text{CuCoO}_x/\text{TiO}_2$ ; carbon monoxide; nitric oxide; catalytic reduction

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### Introduction

Nitric oxide is one of the major air pollutants around the world, consequently, the reduction of NO has become a great challenge in the environment protection. Carbon monoxide is another air pollutant existed in the flue gases and tail gases. Therefore, the reactions between these two compounds might be a novel approach to remove these two toxic components from almost all the emission sources. Numerous reports concerning this subject have been well documented in the past decades, suggesting that both Cu-based and Co-based catalysts were especially promising for the reduction of NO with CO. In a recent research,  $\text{Cu}/\text{TiO}_2$  and  $\text{Cu}/\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$  (Ding *et al.*, 2005) can reach 99% NO conversion at 300 and 225°C, respectively.  $\text{CuO}/\text{CeO}_2$  (Jiang *et al.*, 2003) catalyst can reach 99.8% NO conversion at 250°C.  $\text{CoS}_x$  (Zhang *et al.*, 2003) can keep a steady state with more than 90% NO conversion at 350°C in the presence of  $\text{SO}_2$ . Compared with the former, Cu-Mn/AC (Stankova *et al.*, 2001) and Cu-Co/ $\gamma$ - $\text{Al}_2\text{O}_3$  (Stoyanova *et al.*, 1998) have shown much better activities at low temperatures (below 250°C). However, they have short-comings as well, the disadvantages including too high reaction temperature, bad resistance against  $\text{H}_2\text{O}$  and  $\text{SO}_2$  and so on. Therefore, it is especially important to develop new more effective catalysts working at lower temperature. As was remarked above, copper and cobalt seem to be the effective elements in various catalysts as non-precious metals. Thus, this work was aimed at studying

the catalytic activity toward NO reduction with CO by Cu-Co metal oxides supported by nano- $\text{TiO}_2$  ( $\text{CuCoO}_x/\text{TiO}_2$ ), as nano- $\text{TiO}_2$  has a high surface area and good resistance against  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . As far as we know, the catalyst  $\text{CuCoO}_x/\text{TiO}_2$  has not been used in any reactions between NO and CO.

## 1 Experimental

### 1.1 Preparation of catalysts

Nano- $\text{TiO}_2$ , with a high specific surface area of 120  $\text{m}^2/\text{g}$ , was calcined at 500°C for 5 h before use. All of the catalyst samples were prepared by impregnation method. The stoichiometric aqueous solutions of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and nano- $\text{TiO}_2$  were mixed up and stirred for 2 h at room temperature, then the impregnated solutions were dried in air at 120°C for 5 h. After a slight grind, they were calcined at different temperatures (350, 500, and 600°C). After that, the samples were finely ground and the part of 40–80 mesh was taken for use.

### 1.2 Characterization of the catalysts

The BET specific surface areas of the samples were determined by  $\text{N}_2$  adsorption using a NOVA-1000 Ver.5.01 automated gas sorption system (Malvern Instruments Ltd., UK). X-ray powder diffraction (XRD) patterns were carried out on a Rigaku D/MAX-RAX system (Rigaku Corporation, Japan) with  $\text{CuK}\alpha$  radiation. Temperature programmed reduction (TPR) was performed on Chemi

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Sorb TPR Win v2.0 instrument (Quantachrome, America), the gas used in the measurements was a mixture of 5% H<sub>2</sub>/95% Ar, the temperature ranged from 100 to 700°C and changed at the rate of 10°C/min. All samples should be further ground and dried at 100°C for 2 h before test.

### 1.3 Catalytic test

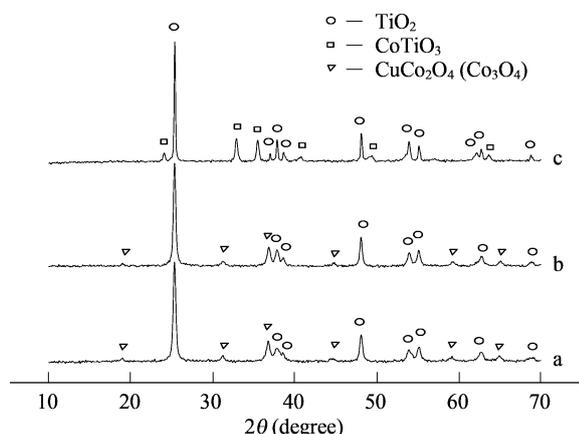
The catalytic activity tests were carried out in a quartz tubular downflow reactor (Schoolrun Factory of Xiangtan University, China) (25 mm in i.d. and 400 mm in length) inserted with a thermometer. Before the measurement, each sample was preheated in a flow of N<sub>2</sub> at 300°C for 1 h, then cooled down to the reaction temperature. The reaction conditions were as follows: 0.1% NO, 1% CO, 4% water vapor (when used), 0.025% SO<sub>2</sub> (when used) in volume, balance N<sub>2</sub> with a total flow rate of 1200 mL/min, and gas hourly space velocities (GHSV) 20000 h<sup>-1</sup> (ambient conditions). Before entering the reactor, the feed gases were mixed in a glass chamber, but CO was feed directly into the reactor by passing the mixing chamber to avoid possible reaction between NO and CO before catalyst bed. The NO and NO<sub>2</sub> concentrations were continually monitored by a chemiluminescent NO/NO<sub>x</sub> analyzer (Model 42C, Thermo Environmental Instruments Inc., USA). All the data were obtained after 60–180 min when the catalytic reaction reached steady state. The calculation method for the NO conversion ( $\eta_{\text{NO}}$ ) is as follows:

$$\eta_{\text{NO}} = (\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}) / \text{NO}_{\text{inlet}} \quad (1)$$

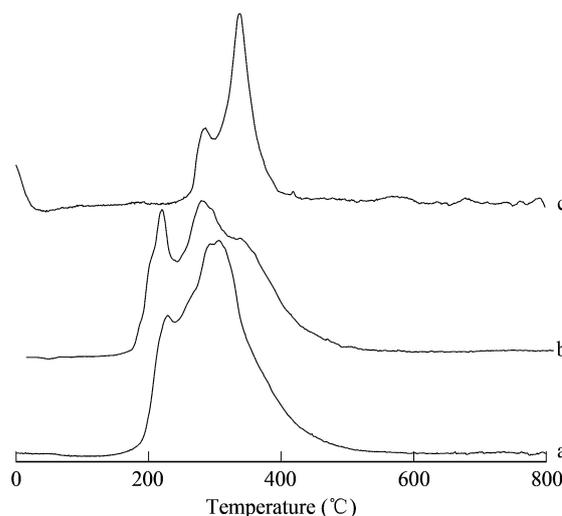
## 2 Results and discussion

### 2.1 Catalyst characterization

The XRD patterns of CuCoO<sub>x</sub>/TiO<sub>2</sub> with Cu/Co = 1/2 in Fig. 1 showed the influence of calcination temperature. The catalysts calcined at 350 and 500°C formed Co<sub>3</sub>O<sub>4</sub> (CoCO<sub>2</sub>O<sub>4</sub>) and CuCoO<sub>4</sub>, respectively, and their diffraction peaks are quite similar with the only difference at 2 $\theta$  = 59° (Hu *et al.*, 2001), which can not be observed by naked eye. However, CuCoO<sub>4</sub> (JCPDS card number 78-2177) will be decomposed partly into CuO and Co<sub>3</sub>O<sub>4</sub> (JCPDS number card 78-1969) above 400°C, whereas Co<sub>3</sub>O<sub>4</sub> will



**Fig. 1** XRD patterns of CuCoO<sub>x</sub>/TiO<sub>2</sub> catalysts calcined at different temperatures. (a) 350°C; (b) 500°C; (c) 600°C.



**Fig. 2** TPR profiles of CuCoO<sub>x</sub>/TiO<sub>2</sub> catalysts. Line a: 350°C; line b: 500°C; line c: 600°C.

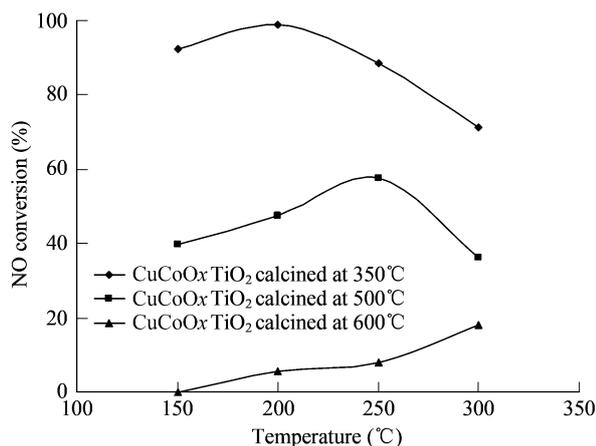
keep steady state below 600°C. Consequently, CuCoO<sub>4</sub> spinel was supposed to exist primarily in sample a, Co<sub>3</sub>O<sub>4</sub> seemed to emerge in sample b. With regard to sample c, CoTiO<sub>3</sub> (JCPDS card number 15-866), a new composition appeared as seen in the pattern, which was formed above 600°C calcinations (Voss *et al.*, 2002). It should be pointed out that no remarkable diffraction peaks assigned to CuO were observed in all the samples for the high dispersion of CuO on TiO<sub>2</sub> or the formation of amorphous phase in the catalyst particles.

The TPR profiles of CuCoO<sub>x</sub>/TiO<sub>2</sub> catalyst samples calcined at 350, 500, and 600°C with Cu/Co = 1/2 are shown in Fig. 2. As compared to sample a, it was quite clear that an additional shoulder peak occurred at 340°C in sample b. Together with results of the XRD and the TPR data, this peak was believed to be the reduction peak of Co<sub>3</sub>O<sub>4</sub> formed at 500°C calcination. And the sample calcined at 600°C had the highest reduction temperature and the highest activation temperature.

The BET results of CuCoO<sub>x</sub>/TiO<sub>2</sub> (Cu/Co = 1/2) catalysts of final calcination at 350, 500, and 600°C were 46.61, 37.78, 10.33 m<sup>2</sup>/g, respectively. CuCoO<sub>x</sub>/TiO<sub>2</sub> calcined at 350°C had the highest surface area of 46.61 m<sup>2</sup>/g, showing the best dispersion of its active species.

### 2.2 Effect of calcination temperature on CO+NO activity

The effect of the calcination temperature of Cu-CoO<sub>x</sub>/TiO<sub>2</sub> on the reduction of NO by CO was studied at reaction temperature ranged from 150 to 300°C. Three catalyst samples were used, each of them with the same total Cu-Co loading of 30% and Cu/Co molar ratio of 1/2. As can be seen in Fig. 3, CuCoO<sub>x</sub>/TiO<sub>2</sub> calcined at 350°C showed the highest catalytic activity compared to the other two, the NO conversion reached 98.9% even at 200°C. However, CuCoO<sub>x</sub>/TiO<sub>2</sub> calcined at 600°C showed the lowest activity for the reaction, and even no activity below 150°C. CuCoO<sub>x</sub>/TiO<sub>2</sub> calcined at 500°C showed poor activity below 300°C, and NO conversion was only 57.5% at 250°C. It should be noted that, CuCoO<sub>x</sub>/TiO<sub>2</sub>

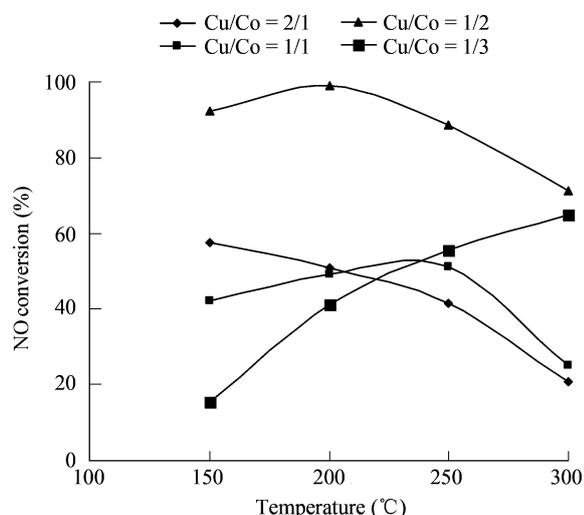


**Fig. 3** NO conversion of CO+NO reaction over CuCoOx/TiO<sub>2</sub> catalysts with different calcination temperatures. Reaction conditions: 0.1% NO, 1% CO, balance N<sub>2</sub>, GHSV = 20000 h<sup>-1</sup>.

calcined at 350°C had formed CuCo<sub>2</sub>O<sub>4</sub> spinel predominantly, which is more active to the reaction of NO and CO than Co<sub>3</sub>O<sub>4</sub> (Muhammad *et al.*, 2008; Stoyanova *et al.*, 1998) and CoTiO<sub>3</sub>. Moreover, it had the largest specific surface area. All of these contribute to its high activity, and Co was considered to be the most important active species in the catalyst too.

### 2.3 Effect of Cu/Co molar ratio on CO+NO activity

Four samples of CuCoOx/TiO<sub>2</sub> were used to study the effect of Cu/Co molar ratio on the catalytic reduction of NO by CO. Each sample has the same Cu-Co total loading of 30% but with a different Cu/Co molar ratio. Cu and Co species must play an integrated role in this catalytic reaction. As shown in Fig. 4, the sample with Cu/Co = 1/2 had an obviously higher activity than the others. This may be due to the ratio Co/Cu = 2 is close to the ratio Co/Cu = 1.855 for the stoichiometric CuCo<sub>2</sub>O<sub>4</sub> (Stoyanova *et al.*, 1998).



**Fig. 4** NO conversion of CO+NO reaction over CuCoOx/TiO<sub>2</sub> catalysts with different Cu/Co molar ratio. Reaction conditions: 0.1% NO, 1% CO, balance N<sub>2</sub>, GHSV = 20000 h<sup>-1</sup>.

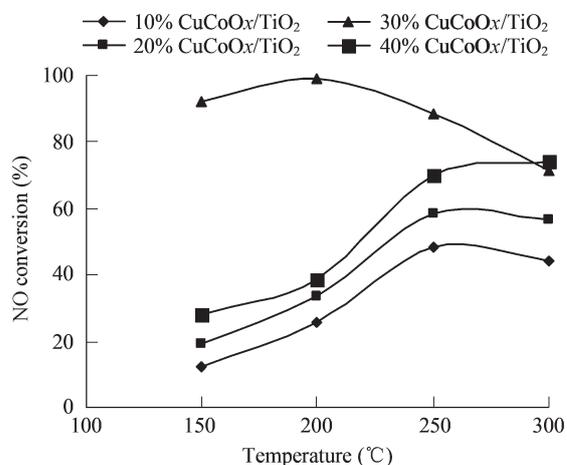
### 2.4 Effect of total loading of Cu-Co on CO+NO activity

There were four CuCoOx/TiO<sub>2</sub> samples with different total loading of Cu-Co had been used to study the effect on CO+NO activity. All of them were calcined at 350°C and had the same Cu/Co ratio of 1/2 with the total Cu-Co loading of 10%, 20%, 30%, 40%, respectively. The experimental results are presented in Fig. 5. In the temperature range from 150 to 300°C, NO conversion was apparently improved with the amount of Cu-Co loading increasing, and reached its highest activity of 98.9% when the Cu-Co loading was 30% at 200°C. When the amount of Cu-Co loading was beyond 30%, the conversion of NO decreased sharply, and the maximum conversion point seemed to shift to more than 300°C. Taken these together, it can be suggested that the optimal amount of Cu-Co total loading on CuCoOx/TiO<sub>2</sub> is 30%.

To further investigate this phenomenon, surface areas of samples with different Cu-Co total loading was measured, and the results are listed in Table 1. It shows that the surface areas of 10% and 20% CuCoOx/TiO<sub>2</sub> are larger than the rests, that may be due to the oxides are highly dispersed over TiO<sub>2</sub>, which inclined to form amorphous phase or crystallite. These particles would interact with the support TiO<sub>2</sub> and the catalytic activity is declined. When the loading exceed 30%, the interaction between the support and Cu-Co oxides becomes feeble and the number of participating surface Cu-Co oxides sites decreases with the loading increasing. Therefore, 30% CuCoOx/TiO<sub>2</sub> is supposed to have the suitable surface area to show the best activity. According to Figs. 3, 4 and 5, CuCoOx/TiO<sub>2</sub> (30%) calcined at 350°C with Cu/Co = 1/2 was considered as the optimum catalyst, which would be used in the

**Table 1** BET specific surface areas with different Cu-Co total loadings

Catalyst sample	Cu-Co load (%)	A <sub>BET</sub> (m <sup>2</sup> /g)
CuCoOx/TiO <sub>2</sub>	10	62.86
CuCoOx/TiO <sub>2</sub>	20	54.13
CuCoOx/TiO <sub>2</sub>	30	46.61
CuCoOx/TiO <sub>2</sub>	40	35.24



**Fig. 5** NO conversion of CO+NO reaction over CuCoOx/TiO<sub>2</sub> catalysts with different Cu-Co total loading. Reaction conditions: 0.1% NO, 1% CO, balance N<sub>2</sub>, GHSV = 20000 h<sup>-1</sup>.

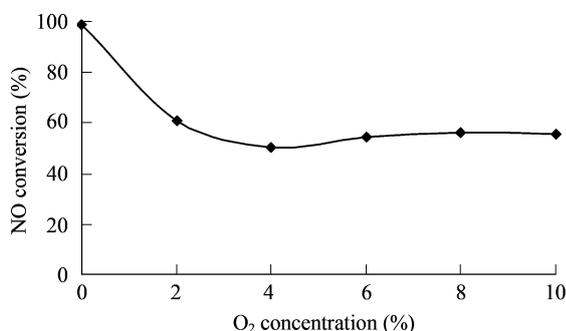
following tests.

### 2.5 Effect of O<sub>2</sub> on CO+NO activity

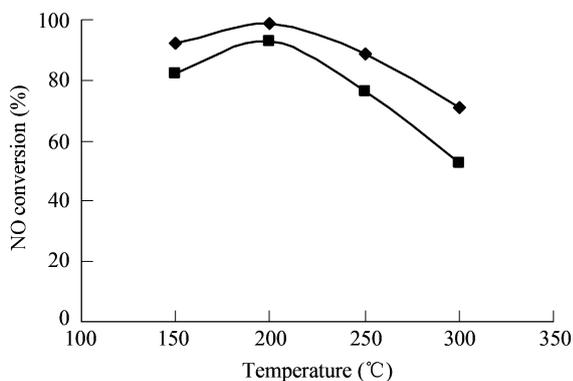
Panayotov *et al.* (1996) reported that low-temperature catalysts for reduction of NO with CO had the problem of deactivation when O<sub>2</sub> was introduced into fed gas. So the effect of O<sub>2</sub> on the activities over CuCo<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> catalyst was studied at 200°C (Fig. 6). The NO conversion dropped to 60.8%–56.2% when 2%–10% O<sub>2</sub> were introduced into the reactor. By comparing with previous publication (Spassova *et al.*, 1999), this phenomenon can be explained that excess O<sub>2</sub> would react with CO and NO to produce CO<sub>2</sub> and NO<sub>2</sub>, the consuming CO reduced the reaction between NO and CO, on the other hand, NO<sub>2</sub> was easier to be reduced to N<sub>2</sub> than NO, and therefore increase the conversion of NO<sub>x</sub> in certain degree. Thus, both competing and accelerating effects of O<sub>2</sub> were observed in this study.

### 2.6 Effect of H<sub>2</sub>O on CO+NO activity

The effect of H<sub>2</sub>O on CO+NO reactions was studied with 4% water vapor being introduced into the bed reactor (Fig. 7). NO conversions decreased to some degree compared to the reaction results without feeding H<sub>2</sub>O at temperatures ranged from 150 to 300°C, this might be correlated with the fact that water vapor has competed with reaction gas in adsorption on the surface of active catalytic sites. Nevertheless, it still could reach 92.7% NO conversion at 200°C. Therefore, CuCo<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> is



**Fig. 6** NO conversion of NO+CO+O<sub>2</sub> over CuCo<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> catalyst. Reaction conditions: 0.1% NO, 1% CO, balance N<sub>2</sub>, GHSV = 20000 h<sup>-1</sup> and reaction temperature of 200°C.



**Fig. 7** Effect of H<sub>2</sub>O on NO conversion over CuCo<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> catalyst. Reaction conditions: 0.1% NO, 1% CO, 4% H<sub>2</sub>O (when used), balance N<sub>2</sub>, GHSV = 20000 h<sup>-1</sup>.

considered to have good water resistance.

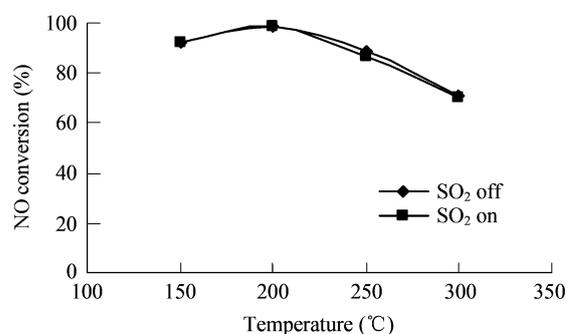
### 2.7 Effect of SO<sub>2</sub> on CO+NO activity

The effect of SO<sub>2</sub> on CO+NO activity was also studied, since residual SO<sub>2</sub> still exists in the flue gases after desulfurization. The results of 0.025% SO<sub>2</sub> fed into the gas can be seen in Fig. 8. Interestingly, the addition of SO<sub>2</sub> had no adverse impact on the NO conversion over CuCo<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub>, which maintained almost 98.9% at 200°C. At each reaction temperature lasting over 3 h, no decrease of conversion was observed. CuCo<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> is supposed to have excellent resistance to SO<sub>2</sub> poisoning. This may be due to the special structure of CuCo<sub>2</sub>O<sub>4</sub> spinel, it has strong adsorption of NO and CO on its extra sites, providing no vacancies for SO<sub>2</sub>. Moreover, reactions between SO<sub>2</sub> and metal oxides in the catalyst are probably too hard to proceed in the absence of H<sub>2</sub>O.

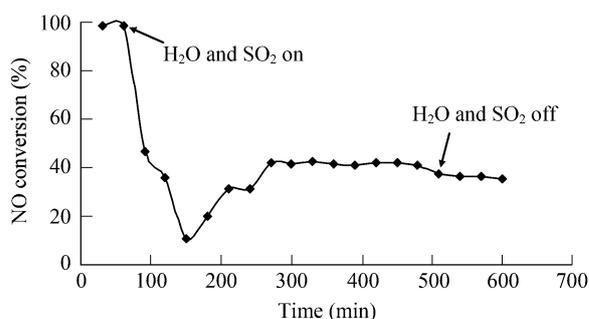
### 2.8 Synergetic effect of H<sub>2</sub>O and SO<sub>2</sub> on CO+NO activity

The presence of both H<sub>2</sub>O and SO<sub>2</sub> on the reduction of NO by CO was further studied at 200°C. It was found that the conversion of NO was greatly declined with 10% H<sub>2</sub>O and 0.025% SO<sub>2</sub> addition (Fig. 9). The conversions of 41.4%–42.8% were obtained. It deserved attention that the NO conversion decreased slightly and stayed at about 36.0% when H<sub>2</sub>O and SO<sub>2</sub> were absent.

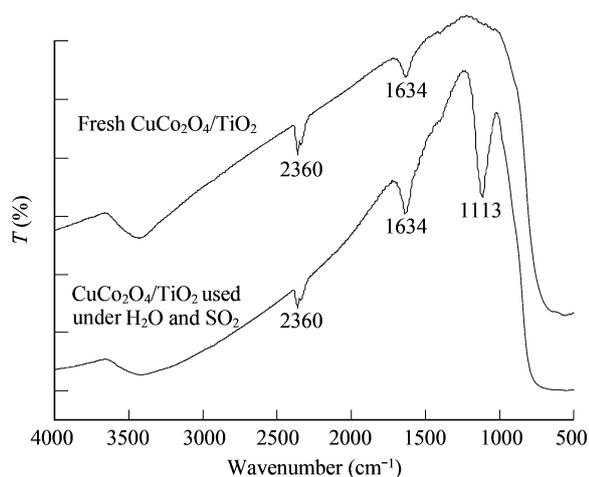
FT-IR spectra of the fresh and used catalysts under H<sub>2</sub>O and SO<sub>2</sub> was performed to understand the deactivation



**Fig. 8** Effect of SO<sub>2</sub> on NO conversion over CuCo<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> catalyst. Reaction conditions: 0.1% NO, 1% CO, 0.025% SO<sub>2</sub> (when used), balance N<sub>2</sub>, GHSV = 20000 h<sup>-1</sup>.



**Fig. 9** Synergetic effect of H<sub>2</sub>O and SO<sub>2</sub> on NO conversion over CuCo<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> catalyst. Reaction conditions: 0.1% NO, 1% CO, 4% H<sub>2</sub>O, 0.025% SO<sub>2</sub>, balance N<sub>2</sub>, GHSV = 20000 h<sup>-1</sup> and reaction temperature of 200°C.

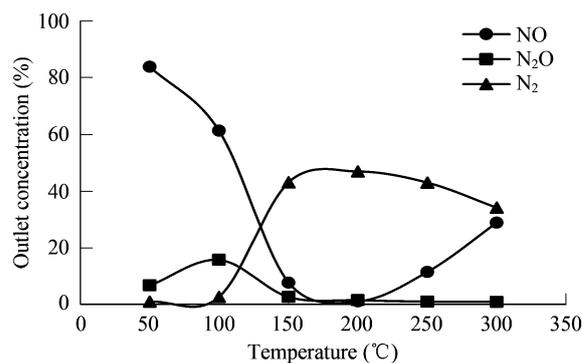


**Fig. 10** FT-IR spectra of the fresh and used under  $\text{H}_2\text{O}+\text{SO}_2$   $\text{CuCo}_2\text{O}_4/\text{TiO}_2$ .

of  $\text{CuCo}_2\text{O}_4/\text{TiO}_2$ . As shown in Fig. 10, the spectrum of the fresh  $\text{CuCo}_2\text{O}_4/\text{TiO}_2$  catalyst displays two IR bands at  $1634\text{ cm}^{-1}$  and  $2360\text{ cm}^{-1}$ , which can be assigned to  $\text{H}_2\text{O}$  and  $\text{CO}_2$  band, respectively. However, the spectrum of used  $\text{CuCo}_2\text{O}_4/\text{TiO}_2$  is similar to that of the fresh one, but a new band appears at  $1113\text{ cm}^{-1}$ , which probably accounts for the existence of  $\text{SO}_4^{2-}$  (Nakamoto, 2009). From these we can infer that, when  $\text{H}_2\text{O}$  and  $\text{SO}_2$  coexist in the feed gas, they would act as  $\text{H}_2\text{SO}_3$  with metal oxides dispersed in  $\text{CuCo}_2\text{O}_4/\text{TiO}_2$  catalyst, and metal sulphates are formed on the catalyst. Then, the active sites are gradually covered by sulphates and the catalyst is irreversibly deactivated. Furthermore, the formed metal sulphates like copper and cobalt sulphates both cannot be decomposed below  $400^\circ\text{C}$ . That is the reason why the NO conversion would not be restored even when  $\text{H}_2\text{O}$  and  $\text{SO}_2$  are removed from the gas. However, the catalyst studied herein still had its practical utilization, it can be used in denitrification of flue gases containing either  $\text{SO}_2$  or  $\text{H}_2\text{O}$ , for example, some gas-fired boiler and oil-fired boiler.

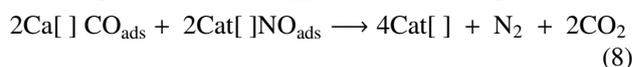
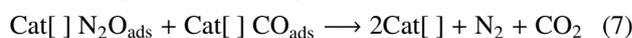
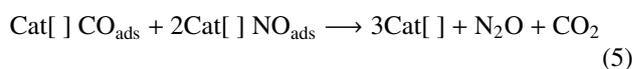
## 2.9 Reaction mechanism of $\text{CO}+\text{NO}$ over $\text{CuCo}_2\text{O}_4/\text{TiO}_2$

To further investigate the mechanism of NO reduction by CO over  $\text{CuCo}_2\text{O}_4/\text{TiO}_2$ , an experiment was carried out at temperatures ranging from  $100$  to  $300^\circ\text{C}$ . In order to accurately measure one of the products  $\text{N}_2$ , Ar was used as balance gas instead of  $\text{N}_2$ . The outlet gas was quantified by GC (GC-14C Gas Chromatograph, Japan). As shown in Fig. 11, NO conversion was very low below  $100^\circ\text{C}$ , while increased when the temperature was rising, and even reached  $98.9\%$  at  $200^\circ\text{C}$ . It was quite confused that NO conversion declined when the temperature continued to increase. It is well known that, reaction rates could be greatly affected by several factors including temperature increase, transmission process and adsorption process. In present study, we believed that NO adsorption, which has become the rate-limiting step above  $200^\circ\text{C}$ , declined and resulted in less NO participated in reactions. Products of reduction reactions were  $\text{N}_2\text{O}$  and  $\text{N}_2$ , and we demonstrated that  $\text{N}_2\text{O}$  was the main product of the reaction between NO and CO



**Fig. 11** The outlet contents of NO,  $\text{N}_2\text{O}$  and  $\text{N}_2$  after  $\text{CO}+\text{NO}$  reaction at different temperatures. Reaction conditions:  $0.1\%$  NO,  $1\%$  CO, balance Ar, GHSV =  $20000\text{ h}^{-1}$ .

below  $100^\circ\text{C}$ , while the majority of  $\text{N}_2$  was determined to produce above  $100^\circ\text{C}$  and reach its theoretical maximal value (nearly  $100\%$ ) at  $200^\circ\text{C}$ . The result was consistent with that reported in many other documents (Gassan-zedeh and Seyidbayova, 2003; Drouet *et al.*, 2001; Jiang *et al.*, 2003; London and Bell, 1973). Reactions between NO and CO over  $\text{CuCo}_2\text{O}_4/\text{TiO}_2$  can be summarized as follows (Gassan-zedeh and Seyidbayova, 2003):



where,  $\text{Cat}[\text{O}]$  represents oxidized catalyst;  $\text{Cat}[\ ]$  means reduced catalyst;  $[\ ]$  means oxygen vacancy; ads means adsorbed state.

## 3 Conclusions

The catalyst  $\text{CuCoO}_x/\text{TiO}_2$  with total Cu-Co loading of  $30\%$  calcined at  $350^\circ\text{C}$  formed Cu-Co spinel and was confirmed to be very effective for reduction of NO with CO at lower temperature. This catalyst showed significantly high activity of  $98.9\%$  NO conversion at  $200^\circ\text{C}$ , but become deactivated rapidly in the presence of  $\text{O}_2$ . It showed good resistance to  $\text{H}_2\text{O}$  or  $\text{SO}_2$  poisoning, but shifted to be less active under the stream containing both  $\text{H}_2\text{O}$  and  $\text{SO}_2$ , NO conversion would not be restored even stopped feeding  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . Mechanism of the NO reduction by CO was also studied in this work,  $\text{N}_2\text{O}$  was mainly yielded below  $100^\circ\text{C}$ , while  $\text{N}_2$  was produced instead at higher temperature and reached its maximum at  $200^\circ\text{C}$ .

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