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Effect of pretreatment atmosphere on CuO/TiO_2 activities in NO + CO reaction

Jiang Xiaoyuan*, Jia Yanrong, Huang Pei Hua, and Zheng Xiaoming

Faculty of Science, Institute of Catalysis, Zhejiang University, Hangzhou, 310028, P. R. China

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Using TiO_2 as carrier, CuO/TiO_2 catalysts with different CuO loading were prepared by the impregnation method. The catalytic activities in NO + CO reaction were examined with a micro-reactor gas chromatography reaction system and the methods of TPR, XPS and NO-TPD. It was found that the catalytic activities were affected by pretreatment atmosphere, i.e. H_2 atmosphere > reduction–reoxidation >10%CO/He > reaction gas (fresh sample). NO decomposition was better by low-valence Cu species than by high-valence Cu species, i.e. $Cu^0 > Cu^+ > Cu^{2+}$. The XPS results indicated that Cu species on CuO/TiO_2 were Cu^0, Cu^+, normal Cu^{2+}(Cu^{2+}(I)) and chain-structured Cu^{2+}(Cu^{2+}(II)) as –Cu–O–Ti–O–. The activities of Cu^{2+}(II) were much higher than that of Cu^{2+}(I), but both species were very unstable in the reaction atmosphere and easily reduced by CO, which accounted for the variable activities of fresh catalysts with increasing reaction temperature. In NO + CO reaction, the redox process was a cycle of Cu^+–Cu^{2+}(I) at low reaction temperature but was a cycle of Cu^0–Cu^+ at high reaction temperature. As shown by NO-TPD, high catalytic activities could be attributed to the following factors, e.g. oxygen caves on the catalyst's surface after pretreatment with H_2 and reduction–reoxidation, formation of Cu^0 after pretreatment with H_2, and increment of Cu species dispersion and formation of Cu^{2+}(II) after pretreatment with reduction–reoxidation.

KEY WORDS: TiO_2; CuO/TiO_2 catalysts; atmospheric pretreatment; NO + CO reactions.

1. Introduction

As the urban air pollution deteriorates due to large amount of unburned hydrocarbon, CO and NO_x, environmental management becomes a major challenge today. As NO_x causes much harm to the environment and human health, effective elimination of NO_x has received much attention such as catalytic reduction of NO_x. Since Iwamoto *et al.* [1,2] reported that hydrocarbon compounds could selectively reduce NO_x in oxygen-rich atmosphere under Cu⁻ZSM5 and other ions exchanged zeolite catalysts, many catalysts have been researched including the most typical CuO/TiO_2 catalysts [3–5]. CuO/TiO_2 catalysts have high activities in deep oxidation of CO and hydrocarbon compounds [6,7] and selective reduction of NO. This kind of catalysts has a very good prospect in purifying flue gases containing NO, CO and harmful organic wastes. It was considered that Cu^{2+} cation's nanometer form was the active phase of catalytic reduction of NO, and similar finding was obtained in NH_3 selectively catalytic reduction of NO. Until now, Cu^{2+} cation on CuO/TiO_2 has been examined with various physical-chemistry methods (ESR, XRD, UV–VIS, XPS and TPR). As shown by IR, ESR and UV–VIS, the stability of Cu^{2+} cation was related to the interaction with oxygen anion in the TiO_2 lattice [8–10]. If Cu^{2+} cations were absorbed on the surface of TiO_2, there would be different co-ordinations between two forms of Cu^{2+} cations and two Lewis acid sites on the surface of TiO_2. The TPR analysis also indicated two forms of Cu^{2+} cations with different reduction abilities [11]. High temperature reduction peak was the reduction of body phase CuO, and low temperature reduction peak was the reduction of Cu^{2+} cation and the interaction of CuO with the carrier. The use of TiO_2 catalysts in the selective reduction of NO has overcome the defaults arising from sulfate formation due to reaction of carrier with SO_x, and thus avoided collapse of carrier structure, assemble of active components and decrease in active surface etc. Therefore, catalytic reduction of NO can be used in a sulphur-containing atmosphere and have high NO conversion activity and N_2 selectivity.

In this study, TiO_2 was used as carrier and the effects of CuO loading on catalytic structures and activities in NO + CO reaction were examined by the methods of TPR, XPS and NO-TPD.

2. Experimental

2.1. Preparation of TiO_2

Hydrolysis took place under the conditions of Ti(O–Bu)$_4$ as a precursor, HCl as an inhibitor and ethanol as solvent. The whole process includes solution, collosol and collogel. The flow rate of fluids changed

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* To whom correspondence should be addressed.
E-mail: xyjiang@mail.hz.zj.cn

dramatically, and a yellow transparent or semitransparent collogel was produced. After resting for 96 h and dried at 60 °C, the samples were calcined for 2 h at 500 °C in air atmosphere and cooled naturally to room temperature to obtain purely white TiO_2 powder.

2.2. *Preparation of catalysts*

Calculated amount of $Cu(NO_3)_2$ solution was soaked with TiO_2 and rested for 12 h. After dried by frying on an electric stove, the mixture was calcined for 2 h at 500 °C in air atmosphere to obtain CuO/TiO_2 catalysts, noted as wt%CuO/TiO_2.

2.3. *Measurements of catalytic activity in NO + CO reaction*

Catalytic activities in NO + CO reaction were measured with a micro-reactor gas chromatography reaction system. The inside diameter of reaction tube was 5 mm. The flow velocity of reaction gas was 30 ml/min, composed of 6% NO and 6% CO, 88% He. Amount of catalysts was 120 mg and air velocity was 5000 h^{-1}. Reactants and products were examined by gas-chromatography thermal conductivity detector. N_2, NO and CO were detected by a 13X molecular sieve column and CO_2 and N_2O detected by a Porapak Q column.

2.4. *Measurements of catalytic properties*

Using H_2-TPR, H_2 consumption was measured in the temperature-rising process by a thermal conductivity detector. The reductive gas was a mixed gas of 95% H_2 and 5% N_2 (v/v). When the base line was stable, TPR experiments were carried out at increasing rate of 15 °C/min.

In XRD, physical phase was measured by a Japanese Rigaku D/Max IIIB automatic X-ray diffraction meter. The CuK_α diffraction sources had an efficiency of 40 kV × 30 mA.

XPS analysis was made by a PHI 5000C ESCA System photoelectron spectrum meter. The excitation sources included AlK_α (14.86.6 eV), MgK_α (1253.6 eV), 12.5 kV and 250 W. The basic pressure was 10^{-8} mbar, and working pressure was 1×10^{-6} mbar. Differentiativity was FWHM Ag3d5/2 = 4 × 104 cps (for metal). The charge effect was calibrated using C1s = 284.6 eV as inside mark.

For NO-TPD measurement, 250 mg samples were transferred into quartz micro-reactor. After pretreatments with He for 0.5 h and H_2 for 1 h at 500 °C, the samples were blown in He for 0.5 h to get rid of excessive NO. Temperature was raised at a rate of 20 °C/min to 600 °C and then the desorption species were examined by mass spectrum.

3. Results and discussion

3.1. *Effect of different pretreatments on activities of CuO/TiO$_2$ in NO + CO reaction*

Twelve percentage of CuO/TiO_2 was pretreated under different conditions to examine the catalytic mechanisms of CuO/TiO_2 in NO + CO reaction. As shown in figure 1, the NO conversion of fresh catalysts reached 100% at reaction temperature of 400 °C (curve 1), but largely increased its low temperature activity (< 300°) after pretreatment with 10%CO/He at 200 °C (curve 2), and in both cases the high temperature activity was unchanged. After pretreatment with H_2 at 500 °C (curve 4), both low and high temperature activities were much higher than samples pretreated with the conditions described above, the NO conversion reached 100% at reaction temperature of 300 °C. After pretreatment with reduction–reoxidation (curve 3), the activity of 12%CuO/TiO_2 was similar to that pretreated in H_2 atmosphere at 500 °C.

3.2. *H$_2$-TPR*

Figure 2 shows the TPR profiles of CuO/TiO_2 catalysts, in which curves (1)–(5) are 12%CuO/TiO_2 catalyst and after reduced in 5% H_2 at 600 °C and reoxided at 400, 300, 200, 100 and 50 °C for 0.5 h; curve (6) is a fresh 6%CuO/TiO_2 catalyst; curve (7) is 6%CuO/TiO_2 pretreated in H_2 at 500 °C for 1 h and then in reaction gas at 400 °C for 2 h at the same temperature; curves (8) and (9) are 6%CuO/TiO_2 pretreated in reaction gas (6% CO, 6% NO and 88% He) at 400 °C for 2 and 0.5 h. It can be seen that from curves (5) to (1), the surface oxygen species were hardly recovered after 12%CuO/TiO_2 oxided at 50, 100 °C for 0.5 h. After reoxidation at 200, 300 and 400 °C, the catalysts had two overlapped peaks and their reduction peak temperatures were lower than un-reoxidated catalyst. The reduction peak area increased with increasing reoxidation temperature, and the peak moved

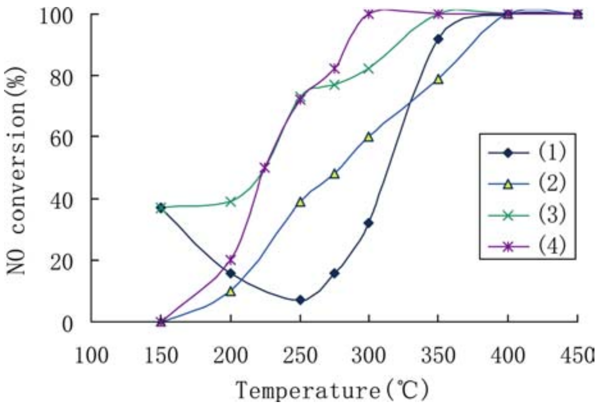

Figure 1. Activity of 12%CuO/TiO_2 with different treatments for NO + CO reaction: (1) fresh catalyst; (2) reduction with 10%CO/He; (3) reduction–reoxidation; (4) reduction with H_2.

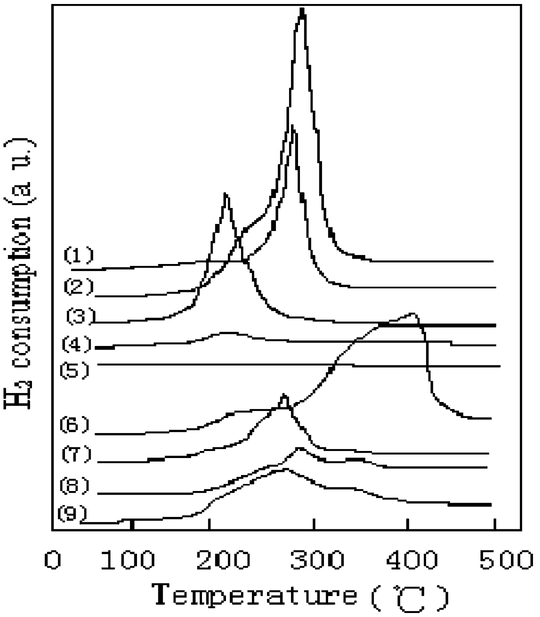

Figure 2. H$_2$-TPR profiles of 12%CuO/TiO$_2$ catalysts.

towards high temperature direction. The reduction peak temperature was 310 °C for 12%CuO/TiO$_2$ reoxided at 400 °C but 365 °C for un-reoxidated catalyst, and the reduction peak area of the former was 1.2 times larger than the latter. This could be due to the change of low valence Cu species into high valence Cu species after reoxidation, which caused an increase in H$_2$ consumption. Reoxidation might also fine the CuO crystal on the surface of carrier and thus decrease the reduction peak temperature. In addition, when the catalyst was pretreated in reaction gas, different peaks (curves (6)–(9)) were seen in TPR analysis, suggesting that 6%CuO/TiO$_2$ still gradually oxided in reaction after pretreatment in H$_2$ at 500 °C, probably as a result of NO oxidation. The results proved that regardless the initial forms of Cu species on 6%CuO/TiO$_2$, Cu species on its surface were always present at a fixed ratio of Cu^0, Cu$^+$ and Cu^{2+} in the end.

3.3. XPS measurement

In order to understand the state and reaction mechanism of CuO/TiO$_2$, we used XPS to measure surface properties of the fresh catalyst and the catalysts pretreated in H$_2$ atmosphere before and after the reaction. Previous studies showed that Cu2p$_{3/2}$ had a main peak at 934.2 eV and a satellite peak between 940 and 945 eV, and that Cu$^+$ had no satellite peak with bonding energy of 1.3 eV lower than Cu^{2+} [12,13]. The bonding energy of Cu^0 was only 0.2 eV lower than that of Cu$^+$ and the two peaks overlapped. Therefore, it was hard to distinguish Cu^0 and Cu$^+$ in terms of bonding energy. However, they can be distinguished by Auger kinetic energy statistics since the kinetic energy was 918.6 eV for Cu^0 and 916.2–917.2 eV for Cu$^+$. Figure 3 shows the bonding energy of Cup$_{3/2}$ of CuO/TiO$_2$.

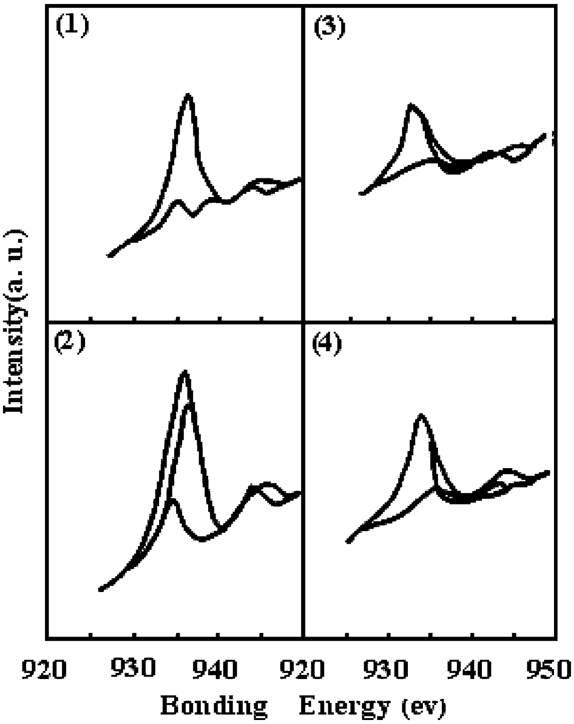

Figure 3. Bonding energy of Cu2p$_{3/2}$ of CuO/TiO$_2$ with different pretreatments: (1) fresh sample; (2) pretreated by reaction gases; (3) pretreated by H$_2$ at 500 °C; (4) pretreated by H$_2$ at 400 °C, then by reaction gases at 400 °C.

Table 1 compares the bonding energy of 12%CuO/TiO$_2$ with different pretreatments. The bonding energies were 932.6 and 934.6 eV, and the major peak occurred at 934.6 eV. After comparing with the standard bonding energies of CuO and Cu$_2$O, it can be suggested that the peak at 932.6 eV represented the low-valence Cu peak. After NO + CO reaction, Cu^{2+}(II) disappeared and Cu^{2+}(I) decreased slightly, and Cu species were mainly as Cu$^+$ with little Cu^0. The XRD analysis showed the existence of Cu^0, which was likely due to the reduction effect of CO in the reaction gas. The results indicated that Cu^{2+}(II) converted to Cu^{2+}(I) and Cu$^+$ in the process of reaction [14–17]. After CuO/TiO$_2$ was pretreated in H$_2$ atmosphere, Cu species were mainly as Cu^0. In contrast, most of Cu^0 converted to Cu$^+$ and Cu^{2+}(I) after pretreatment in reaction gas.

After 12%CuO/TiO$_2$ was pretreated in 10%CO/He or H$_2$ atmosphere, its activity was higher than the fresh catalyst, indicating that Cu^0 had higher reduction property. After a number of reactions, the pretreated catalysts lowered their activities due to the fact that Cu^0 had converted to Cu$^+$ and Cu^{2+}(I), as shown in the XPS results. The XPS results also showed that no matter what pretreatments were, Cu^{2+}(I) and Cu$^+$ co-existed on the catalysts and might involve in NO + CO reaction. This was consistent with the results of TPR measurements. According to the XRD results, Cu species existed mostly as Cu^0 after 12%CuO/TiO$_2$ was pretreated in reaction gas at 500 °C, probably because Cu species

Table 1
The bonding energy of CuO/TiO$_2$ with different pretreatments

Sample	Cu2p$_{3/2}$	B.E.eV		
			O1s	
		Ti2p$_{3/2}$	OH-	O lattice
Cu$_2$O	932.1		531.9	530.2
CuO	934.2		531.8	529.4
TiO$_2$		458.8	531.9	530.1
12%CuO/TiO$_2$(fresh catalyst)	932.6/934.6	458.3	532.4	529.1
12%CuO/TiO$_2$(pretreated by NO + CO reaction gases at 400 °C for 1 h)	932.5/934.5	458.9		530.4
12%CuO/TiO$_2$(pretreated by H$_2$ at 500 °C for 1 h)	932.3/934.2	458.7	533.0	530.6
12%CuO/TiO$_2$(pretreated by H$_2$ at 500 °C for 1 h, then treated by NO + CO reaction gases at 400 °C for 1 h)	932.8/935.6	458.7		530.3

were reduced by CO gas. It may suggest that amount of Cu^0 in the reaction process was related to reaction temperature, i.e. high reaction temperature caused strong atmospheric reduction and more Cu^0 formation on the catalyst's surface [18,19]. In addition, the active Cu species were mainly Cu^0 and Cu$^+$. The findings agreed with that by Hu *et al.* [20, 21], the active components of CuO/CeO$_2$ were Cu^{2+}, Cu$^+$ at 200 °C and Cu$^+$, Cu^0 at 300 °C in NO + CO reaction.

The bonding energy of Ti for pretreated CuO/TiO$_2$ was 458.7 eV, belonging to Ti^{4+} [22]. Ti^{3+} was not detected even under the reduction by H$_2$ at 500 °C. It was likely that the amount of reduced Ti was very little or Ti^{3+} was so active that reoxidation occurred in the reaction. Table 1 also shows that pretreatment in H$_2$ increased the O$_{1s}$ lattice value of the catalyst surface. Fresh CuO/TiO$_2$ had some OH$^-$, and more OH$^-$ formed during cooling after H$_2$ pretreatment [23]. However, OH$^-$ disappeared after pretreatment in reaction gas.

3.4. NO-TPD analysis

Figures 4 and 5 show the NO-TPD profiles of pure TiO$_2$ samples after pretreatments in reaction gases at 400 °C and in H$_2$ at 500 °C. There were two NO absorptions on TiO$_2$ pretreated in reaction gas (figure 4), i.e. two desorption peaks, which occurred at 210 and 295 °C. The first one was a weak absorption and the second one was a strong absorption. Only the weak absorption had the ability of decomposition. When NO desorption took place, N$_2$ and N$_2$O were detected by mass spectrum. After pretreatment in H$_2$ at 500 °C, TiO$_2$ had a third absorption at NO desorption temperature of 80 °C and decomposition effect on NO (figure 5). According to literature, TiO$_2$ readily produced high concentrated n-defection, e.g. the surface Ti^{3+} and O caves under strong reductive atmosphere [24]. O caves increased NO absorption, but Ti^{3+} increased decomposition of NO [25]. It was easy for electrons to transfer from Ti^{3+} to anti-bond orbit of NO, causing NO decomposition [26]. The appearance of the third absorption site proved that Ti^{4+} on the TiO$_2$ surface could be reduced to Ti^{3+} and that Ti^{3+} had better decomposition activity for NO. N$_2$O was detected when NO desorption occurred at reaction temperature of 90 °C. In the whole process of NO-TPD, N$_2$ was not detected, probably due to high original values of N$_2$ so that it was hard to detect small amount of newly formed N$_2$.

After CuO loading (figure 6), the strong absorption site for NO on TiO$_2$ disappeared completely, but the weak absorption site still existed with little change in

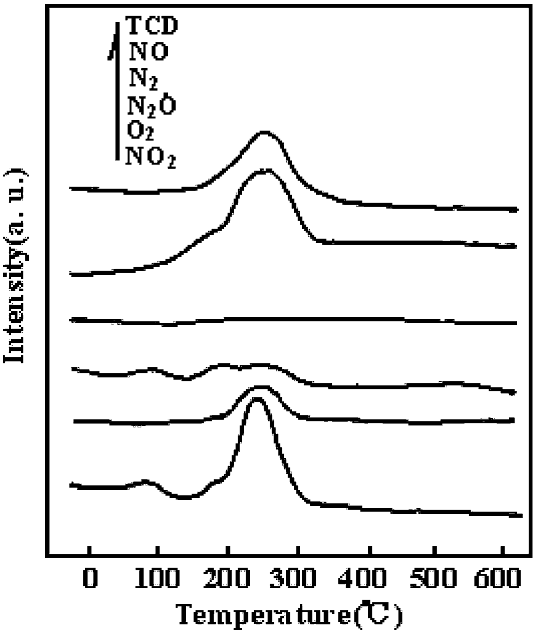

Figure 4. NO-TPD profiles of TiO$_2$ pretreated by reaction gas (6% NO + 6% CO + 88% He).

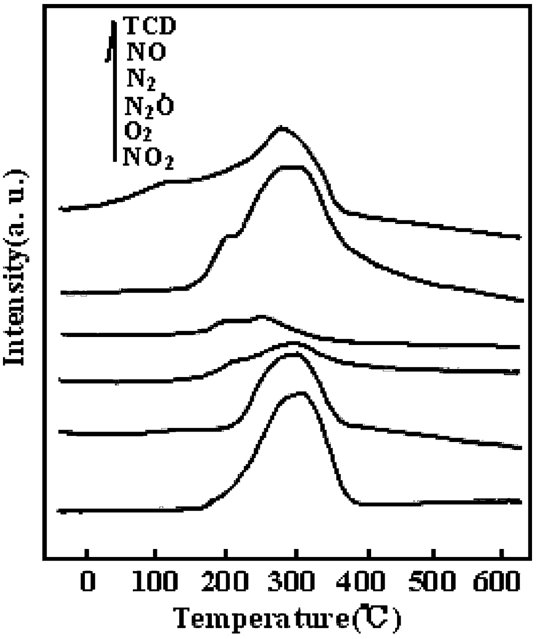

Figure 5. NO-TPD profiles of TiO_2 pretreated by pure H_2.

amount. For 12%CuO/TiO_2, the amount of the second absorption was much more than the third absorption, but was opposite for 3%CuO/TiO_2. This might indicate that the second absorption site was a reductive site of lower-valence Cu. As shown in the TPR results, 12%CuO/TiO_2 was reduced more easily than 3%CuO/TiO_2. Therefore more second absorption sites were available. In addition, the desorption peak temperatures of 3%CuO/TiO_2 and 12%CuO/TiO_2 at the second absorption site had a difference of 15 °C, suggesting that a decrease in CuO loading caused fewer absorption sites and the NO desorption peak and decomposition peak temperature shifted toward high temperature direction. This might account for lower activity of 3%CuO/TiO_2 than that of 12%CuO/TiO_2.

Figure 7 is the signals of NO, N_2O, N_2 NO_2 and O_2, produced in thermal desorption processes after CuO/TiO_2 catalysts were subjected to different pretreatments, which revealed an obvious feature that desorption peak temperature of catalysts pretreated in reductive atmosphere was lower than that pretreated in oxidative atmosphere. According to the NO-TPD results, the pretreatments could be divided into three categories: reductive pretreatment (pretreated by reaction gases, 10%CO/He and pure H_2), oxidation pretreatment (pretreated by reduction–reoxidation) and no pretreatment (pretreated by He). For example, the desorption species of treatments in reductive and oxidation atmosphere at 260 °C were NO, N_2O, N_2, NO_2 and O_2, and their absorption centers did not exist when pretreated in reductive atmosphere. Therefore, the absorption centers of catalysts with different pretreatment at 260 °C were the same species. The desorption species of catalyst pretreatment in He atmosphere were very similar to that of treatments in reaction gases and 10%CO/He, e.g. NO, N_2 and large amount of N_2O, and could be attributed as the same absorption centers.

According to the NO-TPD and XPS results, we can also make the following summaries:

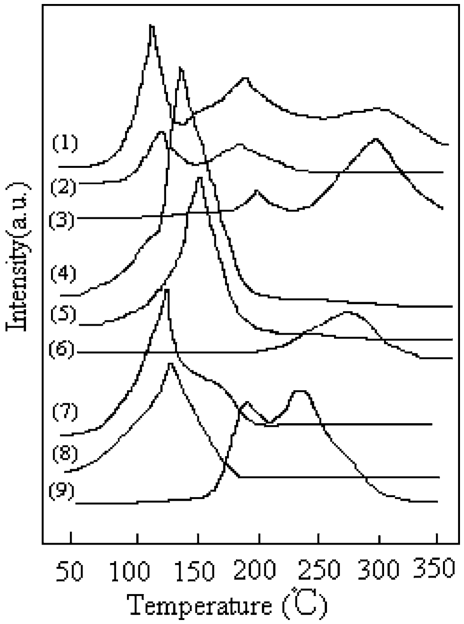

Figure 6. NO (curves 1–3), N_2O (curves 4–6) and N_2 (curves 7–9) signal during NO-TPD processing of CuO/TiO_2 with different CuO loading. Curves (1) (4) and (7) for 12%CuO/TiO_2, curves (2) (5) and (8) for 3%CuO/TiO_2, curves (3) (6) and (9) for TiO_2.

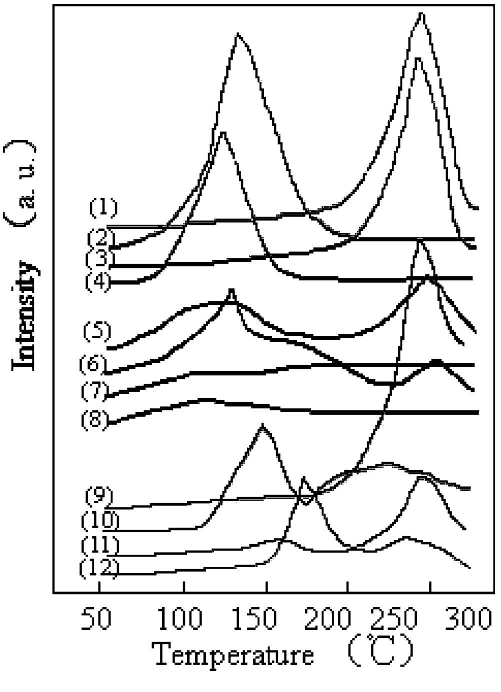

Figure 7. NO (curves 1–4), N_2 (curves 5–8) and N_2O (curves 9–12) signal during NO-TPD processing of CuO/TiO_2 with different pretreatments.

(1) There were three Cu species, i.e. Cu$^+$, Cu^{2+}(I) and Cu^{2+}(II) in the fresh CuO/TiO$_2$. The amount of Cu^{2+}(I) was more than the other two. After pretreatment in reaction gas or reductive gas at high temperature, Cu^{2+}(II) converted to Cu$^+$ and Cu^{2+}(I). Eventually, Cu species existed mainly as Cu$^+$ and Cu^{2+}(I). Cu^0 formation occurred at high reaction temperature. The results indicated that the active Cu species were Cu$^+$ and Cu^{2+}(I) at low reaction temperature, and Cu^0 and Cu$^+$(I) at high reaction temperature. Cu^{2+}(II) species possessed very high activity [26]. The XPS results showed that the activity of catalysts pretreated in reaction gases Cu^{2+}(II) species disappeared after reaction. Catalysts of pretreatment by reduction–reoxidation had more Cu^{2+}(II), which contributed to high activity. In addition, the existence of oxygen vacancy and Ti^{3+} was another factor in increasing activity.

(2) Komova *et al.* [26] considered that Cu^{2+} first coordinated with low-coordinated O atom in lattice when CuO concentration was low, and a chain structure formed. The chain length was related to Cu^{2+} number, and the bonding energy of low-coordinated O atom was relatively high. After pretreated in reaction gas, Cu^{2+}(II) and O species with high bonding energy disappeared at the same time, indicating that they bonded together.

(3) The TPD results indicated that Cu$^+$ had the ability of absorbing NO. Most literature suggests that Cu$^+$ absorbs both NO and CO and thus the NO absorption by Cu$^+$ may be hindered. By comparison, NO is readily absorbed by Cu^{2+} or Cu^0 [27]. Wu *et al.* [28] reported that the lower the valence of metallic cations, the more likely "$M^{(n+1)+} \rightarrow O^-$"occurred, e.g. Cu$^+$ had a strong activating effect on NO: $Cu^+ + NO \rightarrow [Cu^+\text{-}NO^-]$. Since the bond energy of N=O in NO$^-$ was lower than that of N-O in NO and NO$^+$, the N=O bond was easier to break. Our results also showed that the lower the valence of Cu, the lower temperature was needed for NO decomposition. The ability of NO activation by Cu species was $Cu^0 > Cu^+ > Cu^{2+}$. One of the reasons that CuO/TiO$_2$ had high activity after pretreatment in CO and H$_2$ was the existence of Cu^0. In addition, the oxygen caves contributed to high catalytic activity.

(4) Two possibilities may account for less amount of NO desorbed by the H$_2$-reduced catalyst than by other catalysts. First, the reductive effect of H$_2$ was greater than that of CO and NO + CO. Therefore, the Cu grains produced by the H$_2$-reduced catalyst were bigger than by the catalysts reduced in CO or NO + CO, and thus the former had less absorption than the latter. Gandhi *et al.* [29] found large amount of Cu^{2+} and Cu^0 on pre-oxidized and pre-reduced CuO/Al$_2$O$_3$, respectively, but little Cu$^+$ in both catalysts. Similar results were reported by Hierl *et al.* [30]. However, our findings were quite different. In TPD process, there were only three peaks of the catalysts either reductively pretreated or oxidatively pretreated. By including infrared analysis, these three peaks were believed to be the desorption of Cu^{2+}-NO, the second desorptions of new species Cu$^+$-ONO$^-$ and Cu$^+$-ONO$_2^-$. In the whole desorption process, Cu^0 and Cu$^+$ were not involved because Cu^0 had been oxidized in the process of NO absorption, but the rate of NO absorption by Cu$^+$ was very slow, so its signal in infrared spectrum was very weak.

(5) The following qualitative information could be obtained by TPD: e.g. absorption types (active center), absorption strength (energy), reactions of absorbing molecule and solid surface, and the surface structure [31]. Moreover, NO-TPD process demonstrated that whatever pretreatments (e.g. He blowing at high or low temperature, H$_2$ reduction) could not replace the role of catalysts in NO + CO reaction. In order to have a close relationship between the TPD results and reaction activity, proper pretreatments are needed. The results of pretreatment with CO gas were very similar to that with NO + CO reaction gas. CO pretreatment in NO-TPD process could simulate real CuO/TiO$_2$ situation on the catalyst's surface in NO + CO reaction.

4. Conclusion

(1) The activity of CuO/TiO$_2$ with different pretreatments can be listed as: pretreatment in H$_2$ atmosphere > reduction–reoxidation pretreatment > CO reductive pretreatment > reaction gases pretreatment (fresh sample). The lower the Cu valence, the lower the reaction temperature needed for NO decomposition. The activity for NO decomposition was $Cu^0 > Cu^+ > Cu^{2+}$.

(2) Cu species of CuO/TiO$_2$ included CuO, Cu$^+$, normal Cu^{2+} (i.e. Cu^{2+}(I)) and chain structured Cu^{2+} (i.e. Cu^{2+}(II)) as –Cu–O–Ti–O–. Cu^{2+}(II) had much higher activity than Cu^{2+}(I), but both were very unstable and could be easily reduced by CO in reaction gas. This explained the fluctuations in activity of fresh catalysts with rising reaction temperature.

(3) In reaction, the amount of Cu^0 in CuO/TiO$_2$ catalysts was mainly determined by reaction temperature. The higher reaction temperature was, the more Cu^0 produced. Redox process was carried out by the Cu$^+$–Cu^{2+}(I) cycle when reaction temperature was lower but by Cu^0–Cu$^+$ cycle when reaction temperature was higher.

(4) After pretreatment in H$_2$ and redox process, O vacancy formed on catalyst's surface and contributed to increasing activity. High activity by H$_2$

reduction might be due to the formation of Cu^0. Catalysts with redox pretreatment also showed high activity as a result of increase in dispersity of Cu species and formation of Cu^{2+}(II).

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