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Catalytic activities of CuO/TiO_2 and $CuO\text{-}ZrO_2/TiO_2$ in NO + CO reaction

Jiang Xiaoyuan [a,*], Ding Guanghui [a], Lou Liping [b], Chen Yingxu [b], Zheng Xiaoming [a]

[a] *Institute of Catalysis, Faculty of Science, Zhejiang University, Hangzhou 310028, PR China*
[b] *Institute of Environmental Engineering, Faculty of Environment and Resource, Zhejiang University, Hangzhou 310029, PR China*

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Abstract

CuO/TiO_2 and $CuO\text{-}ZrO_2/TiO_2$ catalysts with different CuO loadings were prepared by the impregnation method using $Cu(NO_3)_2$ and $Ce(NO_3)_3$ aqueous solutions of desired concentrations. The catalytic activities in NO + CO reaction were investigated, and the structural and reductive properties of various CuO/TiO_2 and $CuO\text{-}ZrO_2/TiO_2$ catalysts were characterized by means of BET, TPR, XRD and NO-TPD technology. It was found that after treatment in H_2 at 500 °C for 2 h, the catalytic activities were improved dramatically compared with treatment in normal air at 500 °C for 2 h. The NO conversion temperature ($T_{99\%}$) was 325 °C for 6% CuO/TiO_2 and 300 °C for 6% CuO-10% ZrO_2/TiO_2, and their activities increased with increase in ZrO_2 loading. There were four TPR peaks in CuO/TiO_2 and two TPR peaks in $CuO\text{-}ZrO_2/TiO_2$, indicating that addition of ZrO_2 caused changes in CuO species on TiO_2. The air-treated catalysts displayed CuO diffraction peaks, whereas the H_2-treated catalysts displayed Cu metal diffraction peaks. Four desorption species (NO, N_2O, N_2 and O_2) were detected during the thermal desorption of NO by CuO/TiO_2 and $CuO\text{-}ZrO_2/TiO_2$ treated in both air and H_2. There were two adsorption states of nitric oxide (NO) on the catalyst's surface, i.e. desorption species at low temperature on the weak sites and at high temperature on the strong sites. Addition of ZrO_2 onto CuO/TiO_2 shifted the NO dissociation peaks towards low temperature, which means that the activity of NO decomposition was higher by $CuO\text{-}ZrO_2/TiO_2$ than by CuO/TiO_2. The NO + CO reaction formed intermediary product N_2O at low temperature but formed N_2 at high temperature. In addition, the peak temperature of NO desorption corresponded with the catalyst's activity under both air and H_2, and the dissociation of NO on catalyst surface was a rate-determining step in NO + CO reaction.

Keywords: CuO/TiO_2 and $CuO\text{-}ZrO_2/TiO_2$ catalysts; NO + CO reaction; NO-TPD

1. Introduction

Nitric oxide (NO) is one of the major air pollutants particularly in the modern large cities. It is estimated that $35–38 \times 10^6$ tonnes of NO are released from the exhaust gases of automobiles every year in the world. NO causes severe environmental hazards and is very harmful to the health of human being. The common methods of NO treatment include liquid or solid absorption, selective catalytic reduction of NO with NH_3 and electronic irradiation. However, all these methods result in incomplete NO treatment and cause secondary pollutions. Since 1980s, scientists have been looking for highly efficient $DeNO_x$ catalysts to eliminate NO through reductive mechanism. In early 1989, Iwamoto et al. [1,2] found that Cu-ZSM5 catalyst had much better catalytic activity for NO dissociation. Since then, catalytic reduction of NO has been extensively studied and variety of transition and noble metal catalysts were prepared [3,4]. In recent years, use of TiO_2 as catalyst's carrier has attracted much attention and TiO_2-based catalysts are widely applied in NO reduction [5–8]. TiO_2-based catalysts overcome the shortcoming of TiO_2 and SO_x interaction that produces sulphate and causes structural collapse of the carrier, particle gathering of active components and reduction of active surfaces. As a result, the catalytic reduction of NO can be achieved in a sulphur-containing atmosphere, and obtain an excellent NO conversion and N_2 selectivity.

Various physicochemical methods are also used to investigate the state of copper ion in CuO/TiO_2 catalysts, and inconsistent results have been reported. Komova et al. [7] found that TiO_2-supported CuO could exist as Cu^{2+} ions,

* Corresponding author. Tel.: +86-571-88273272.
E-mail address: xyjiang@mail.hz.zj.cn (J. Xiaoyuan).

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bulk CuO, chain stabilized Cu^{2+} ions, and two different oxide clusters with a structure similar to CuO. In contrast, Xu et al. [8] reported two Cu^{2+} ions with significantly different reducibility on the anatase surface—CuO phase and highly-dispersed Cu^{2+}, similar to CuO/γ-Al_2O_3. Larsson et al. [9,10] suggested that low temperature peak in Cu3–Ti of the H_2-TPR profiles was monomeric copper containing Cu^{+}, and that in Cu12–Ti was polymeric copper containing Cu^{2+}. They also found that catalysts using TiO_2 as carrier displayed a high catalysis in CO oxidation, and that CuO catalyst had much higher activity than MoO_x, FeO_x and CoO_x catalysts and its activity at low temperature was even superior to Pt/γ-Al_2O_3 catalyst.

In this study, reducibility and characteristics of the catalysts were investigated using the methods of BET, TPR, XRD and NO-TPD. ZrO_2 was added onto CuO/TiO_2 to examine the catalyst's activity and stability in NO + CO reaction.

2. Experimental

2.1. TiO_2 preparation

TiO_2 was prepared by sol–gel method from $TiCl_4$ with ammonia solution as precipitating agent and ethanol as dispersing agent. $TiCl_4$ of 25 ml was dissolved in 20 ml distilled water in an ice–water bath. The titanium solution was then slowly mixed with 30 ml distilled water and 20 ml ethanol, and ammonia was added dropwise until pH = 9. During ammonic addition an intensive precipitation occurred. After the solvent was evaporated at 80 °C for 24 h, the precipitates were dried at 300 °C for 2 h to remove NH_4Cl, and then calcined in an air stream of 450 °C for 4 h.

2.2. Catalyst preparation

The CuO/TiO_2 and CuO-ZrO_2/TiO_2 catalysts were prepared by the impregnation method using $Cu(NO_3)_2$ and $Zr(NO_3)_4$ aqueous solutions of desired concentrations. These catalysts were dried at 120 °C for 2 h, followed by calcinations in an air stream of 500 °C for 2 h. They were denoted as w% CuO/TiO_2 and w% CuO-w'% ZrO_2/TiO_2, where w and w' are the amount of CuO and ZrO_2 loading, respectively.

2.3. Measurements of catalytic characters

The BET surface area of catalysts was determined by N_2 adsorption at 77 K using a Coulter OMNISORP-100 instrument.

H_2-temperature programmed reduction (TPR) was done by gas chromatography (GC) using a thermal conductivity detector. The sample (5–10 mg) was activated in an O_2 stream at 500 °C for 0.5 h. After it was cooled to 30 °C, H_2-TPR was conducted. The reduction gas contained 5% H_2 and 95% mixture of H_2 and N_2 at 99.999% purity. Both H_2 and N_2were purified using a 401 deoxidiser and silica gel. The flow rate of the H_2/N_2 mixture was 18 ml min^{-1} (β = 20 K min^{-1}).

X-ray diffraction (XRD) data were obtained at 25 °C using a horizontal Rigaku B/Max lllB powder diffractometer with Cu Kα radiation and a power of 40 × 30 mA. The diffraction angles were 2θ (°). The wavelength of the source used was Cu Kα = 1.540598 Å.

To measure NO-temperature programmed desorption (TPD), 250 mg of fresh catalysts were loaded onto a quartz reactor (Φ = 5 mm) and reduced in H_2 atmosphere at 500 °C for 1 h, and followed by two treatments. In treatment one, catalysts were heated in He at 600 °C for 1 h, and then cooled to 40 °C in a flow of He and exposed to a 10% NO–He mixture gas. Excessive NO was removed, and the catalysts were kept in He flow until no significant amount of adsorbates could be detected. The catalysts were then ramped at 600 °C at a linear heating rate of 20 °C min^{-1} in He flow. The effluent gases were analyzed with a mass spectrometer. In treatment two, after the catalysts were heated in He at 500 °C for 1 h, the following procedures were the same as those in treatment one.

2.4. Measurements of catalytic activity in NO + CO reaction

Catalytic activity was determined under the steady state in a fixed-bed quartz reactor (6 mm). The particle size of catalysts was 20–40 mesh, and 120 mg of the catalysts were used. The reaction gas (i.e. feed steam) consisted of a fixed composition of 6.0% NO, 6.0% CO and 88% He (v/v) as a dilute. The catalysts were treated using either H_2 or air at 500 °C for 1 h. After the catalysts were cooled to room temperature, they were allowed to react with the mixed gas. The reactions were operated at different temperatures at a space velocity of 5000 h^{-1}. Two columns and thermal conduction detectors were used for analyzing the catalytic activity. Column A was packed with 13X molecular sieve for separating N_2, NO and CO, and Column B was packed with Paropak Q for separating N_2O and CO_2 (Fig. 1). The catalytic activity was calculated using the following formula

$$[NO]_{conv} = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}}$$

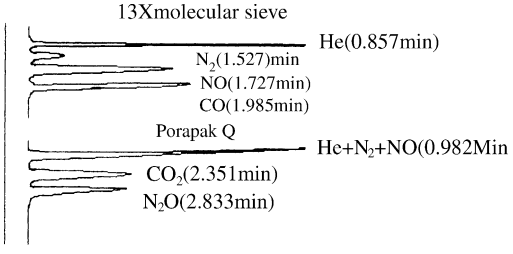

Fig. 1. Separation of reaction products by gas chromatography.

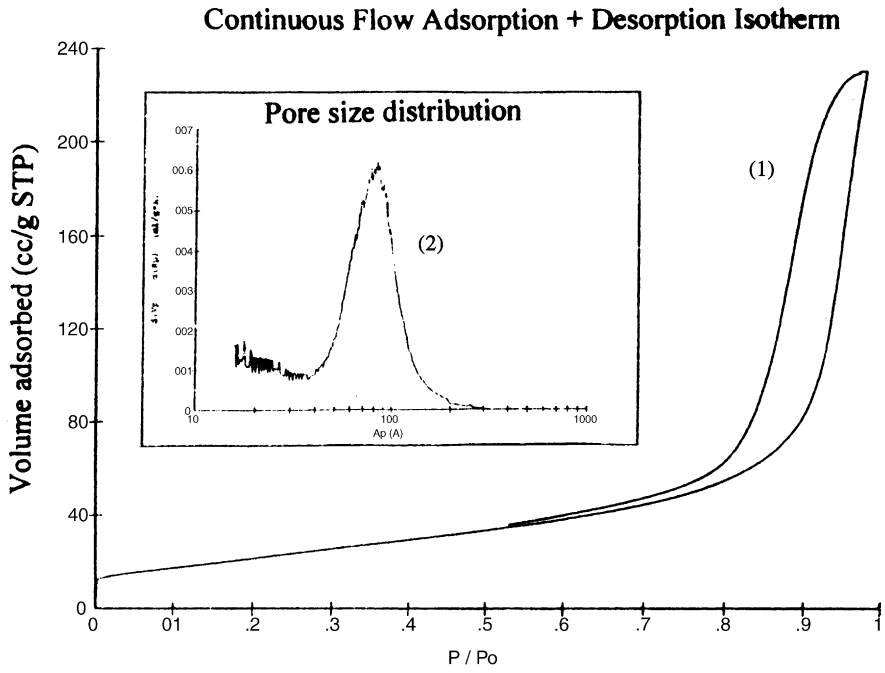

Fig. 2. Adsorption–desorption isotherm and pore-size distribution of TiO_2. (1) Adsorption–desorption isotherm. (2) Pore-size distribution.

$$[N_2]_{set} = \frac{2[N_2]}{[NO]_{in} - [NO]_{out}}$$

3. Results and discussion

3.1. Textural and structural properties of TiO_2

Nitrogen adsorption–desorption by TiO_2 was examined in order to estimate its specific surface area and porosity. The results showed that the material of TiO_2 was porous and the N_2 isotherm of TiO_2 was of type IV, typical of a mesoporous sample (Fig. 2). Pore-size distribution curves calculated from the desorptive branch of the isotherm also indicated the presence of mesoporosity although they were not regularly ordered pores. The specific surface area and total pore volume of TiO_2 were $80.7\,m^2\,g^{-1}$ and $3.884 \times 10^{-1}\,ml\,g^{-1}$. Average pore diameter and stochastic pore diameter were 19.2 and 7.0–9.0 nm, respectively.

TG-DTA analysis of TiO_2 showed an absorption heat peak around 100 °C when it was heated at a liner rate of $20\,°C\,min^{-1}$ from 50 to 800 °C. This peak could be due to the evaporation and removal of adsorbed H_2O. An exothermic peak was also observed around 400 °C, indicating the completion of anatase crystallization. There were no exothermic peaks above 400 °C, suggesting that anatase transformation was a gradual process. In addition, a step of weightlessness was evident in the section of TG curve from 100 to 250 °C (Fig. 3).

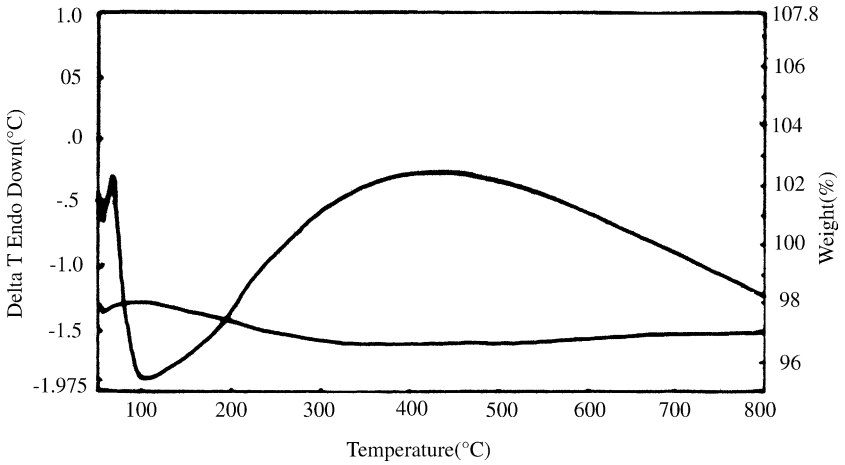

Fig. 3. TG-DTA patterns of TiO_2.

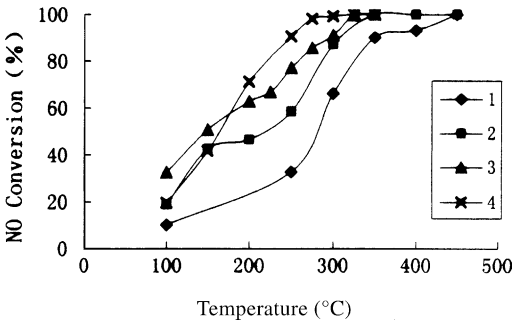

Fig. 4. Catalytic activities in NO+CO reaction under two atmospheres (1) 6% CuO/TiO_2 (air atmosphere); (2) 6% CuO-10% ZrO_2/TiO_2 (air atmosphere); (3) 6% CuO/TiO_2 (H_2 atmosphere); (4) 6% CuO-10% ZrO_2/TiO_2 (H_2 atmosphere).

3.2. Effects of CuO/TiO_2 and $CuO\text{-}ZrO_2/TiO_2$ on NO + CO reaction

As shown in Fig. 4, the activities of 6% CuO/TiO_2 and 6% CuO-10% ZrO_2/TiO_2 catalysts in H_2 atmosphere were much better than that in air atmosphere. The NO conversion temperature ($T_{99\%}$) was 325 °C in H_2 and 450 °C in air for 6% CuO/TiO_2 catalyst. The activity order of 6% CuO-10% ZrO_2/TiO_2 catalysts was the same as 6% CuO/TiO_2 in both H_2 and air, but $T_{99\%}$ was 300 °C in H_2 and 350 °C in air. This might indicate that the addition of ZrO_2 increased catalytic activity in NO + CO reaction in both atmospheres.

3.3. Activities in NO + CO reaction by catalysts calcined at 750 and 850 °C

The activities of $CuO\text{-}ZrO_2/TiO_2$ catalysts calcined at 750 °C for 2 h were similar to those calcined at 500 °C for 2 h in air atmosphere but decreased dramatically after calcination at 850 °C for 2 h (Fig. 5). The activity reduction was likely due to the fact that the heat stability of CuO could not maintain at 850 °C, which caused the gathering of active copper species. The NO conversion temperatures

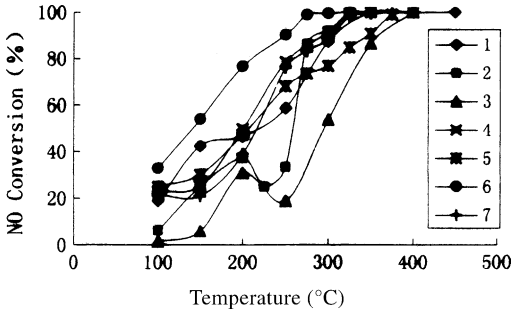

Fig. 5. NO + CO reaction by catalysts heated at 750 and 850 °C. (1) 6% CuO-10% ZrO_2/TiO_2 (500 °C, air atmosphere); (2) 6% CuO-10% ZrO_2/TiO_2 (750 °C, air atmosphere); (3) 6% CuO-10% ZrO_2/TiO_2 (850 °C, air atmosphere); (4) 6% CuO-5% ZrO_2/TiO_2 (500 °C, H_2 atmosphere); (5) 6% CuO-5% ZrO_2/TiO_2 (750 °C, H_2 atmosphere); (6) 6% CuO-10% ZrO_2/TiO_2 (750 °C, H_2 atmosphere); (7) 6% CuO-15% ZrO_2/TiO_2 (750 °C, H_2 atmosphere).

($T_{99\%}$) for 6% CuO-5% ZrO_2/TiO_2 were 325 °C and 400 °C after the catalyst was calcined at 500 °C and 750 °C for 2 h in H_2 atmosphere, respectively. $T_{99\%}$ was also 325 °C for 6% CuO-10% ZrO_2/TiO_2 but increased to 350 °C for 6% CuO-15% ZrO_2/TiO_2 after both catalysts were calcined at 750 °C for 2 h, indicating that catalytic activities decreased with increase in ZrO_2 loading. The findings may suggest that there was a critical amount of ZrO_2 loading. When 5% ZrO_2 was loaded, anti-high temperature property was not clear. When ZrO_2 loading increased to 15%, catalytic activity and heat stability decreased slightly.

3.4. Effect of temperature on NO, CO conversion and N_2 selectivity

As shown in Tables 1 and 2, the activities of 6% CuO/TiO_2 and 6% CuO-10% ZrO_2/TiO_2 catalysts were better in H_2 than in air. NO and CO concentrations decreased simultaneously, but N_2 and CO_2 increased with increase in reaction temperatures under both atmospheres. When the catalysts were treated in air at 150 °C, the amount of N_2, CO_2 and N_2O released from NO and CO conversions increased markedly. A continuous increase in N_2 and CO_2 but a decrease in N_2O was observed at 200 °C. At 300 °C, NO and CO conversions were 66.7 and 70.6% by 6% CuO/TiO_2 and 87.2 and 53.8% by 6% CuO-10% ZrO_2/TiO_2, respectively. At 350 °C, NO and CO conversions reached 99.6% by 6% CuO-10% ZrO_2/TiO_2 compared with 91.3 and 85.6% by 6% CuO/TiO_2. When the catalysts were treated in H_2 at 300 °C, the NO + CO reaction appeared to be complete (100%) by 6% CuO-10% ZrO_2/TiO_2, whereas NO and CO conversions were 91.3 and 85.5% by 6% CuO/TiO_2, respectively. These results indicated that N_2O was formed during the initial stage of the reaction at lower temperatures, and the amount of N_2O increased with increase in temperature until a maximum of N_2O was reached. Further increase in temperature, however, caused a gradual decrease in N_2O until reaching zero. In contrast, the amount of N_2 increased continuously with increase in temperature. Therefore, it can be suggested that in the process of NO reduction with CO, the reactant molecules NO and CO were first adsorbed on the adsorption sites of catalyst surface in form of $NO_{(a)}$ and $CO_{(a)}$, and the adsorbed NO was then dissociated into $N_{(a)}$ and $O_{(a)}$, followed by reactions of $N_{(a)}$ with $NO_{(a)}$ and $CO_{(a)}$ with $O_{(a)}$ to produce $N_2O_{(a)}$ and CO_2, and N_2 formation by two $N_{(a)}$. This study also shows that the rate of $NO_{(a)}$ dissociation on the catalyst surface was slower at low temperature and its reaction with $N_{(a)}$ formed $N_2O_{(a)}$. As the reaction temperature increased, the rate of $NO_{(a)}$ dissociation became faster, causing a reduction of $NO_{(a)}$ concentration. As a result, high temperature was not beneficial to N_2O formation. Therefore, effects of the catalysts on the NO + CO reaction were not only related to the dispersion state of active components CuO on TiO_2 but also to the rate of NO dissociation on the catalyst surfaces.

The elementary steps involved in NO + CO reaction are widely accepted as the following equations [11], where S

Table 1
Effect of temperature on NO, CO conversion and N_2 selectivity in NO + CO reaction by catalysts treated in air atmosphere

Temperature (°C)	Conversion (%)				N_2 Selectivity	
	6% CuO/TiO_2		6% CuO-10% ZrO_2/TiO_2		6% CuO/TiO_2	6% CuO-10% ZrO_2/TiO_2
	NO	CO	NO	CO		
150	30.8	21.9	42.3	21.5	13.7	0
200	35.3	21.9	46.4	25.0	10.1	9.26
250	40.9	23.0	58.5	30.2	15.9	43.9
300	66.7	70.6	87.2	53.8	65.7	91.9
350	91.3	85.5	99.6	96.3	78.4	100
400	91.8	85.2	100	99.3	100	100
450	99.0	90.2	100	100	100	100
500	100	97.3	100	100	100	100

Table 2
Effect of temperature on NO, CO conversion and N_2 selectivity in NO + CO reaction by catalysts treated in H_2 atmosphere

Temperature (°C)	Conversion (%)				N_2 Selectivity	
	6% CuO/TiO_2		6% CuO-10% ZrO_2/TiO_2		6% CuO/TiO_2	6% CuO-10% ZrO_2/TiO_2
	NO	CO	NO	CO		
100	32.4	23.1	19.5	18.3	45.9	28.3
150	50.7	37.2	41.5	35.9	69.4	45.9
200	62.7	53.2	71.2	58.9	100	100
250	77.1	70.9	90.6	76.5	100	100
275	85.5	79.0	98.1	83.2	100	100
300	91.1	85.3	99.2	87.5	100	100
325	99.6	87.9	100	100	100	100
350	100	89.9	100	100	100	100

denotes adsorption sites of catalyst surface, and (a) denotes adsorption state,

$$CO + S \rightarrow CO_{(a)} \quad (1)$$

$$NO + S \rightarrow NO_{(a)} \quad (2)$$

$$NO_{(a)} + S \rightarrow N_{(a)} + O_{(a)} \quad (3)$$

$$CO_{(a)} + O_{(a)} \rightarrow CO_2 + 2S \quad (4)$$

$$NO_{(a)} + N_{(a)} \rightarrow N_2O_{(a)} + S \quad (5)$$

$$N_2O_{(a)} \rightarrow N_2O + S \quad (6)$$

$$N_2O_{(a)} \rightarrow N_2 + O_{(a)} \quad (7)$$

$$N_{(a)} + N_{(a)} \rightarrow N_2 + 2S \quad (8)$$

These equations may also explain the mechanisms of thermal decomposition of NO on the 6% CuO/TiO_2 and 6% CuO-10% ZrO_2/TiO_2 catalysts in this study. At low temperature, the reaction rate of steps (3) and (8) were very slow, and most of $NO_{(a)}$ existing on the catalyst surface formed N_2O through steps (5) and (6). At high temperature, the reaction rate of step (3) was very fast and there were very few $NO_{(a)}$ on the catalyst surface. N_2O was likely to be decomposed at high temperature, and therefore the higher reaction temperature was, the higher the selectivity of NO + CO reaction was.

3.5. H_2-TPR of catalysts

Fig. 6 shows the TPR profiles of pure CuO, TiO_2, 3% CuO/TiO_2 and 6% CuO/TiO_2 catalysts. A single peak was

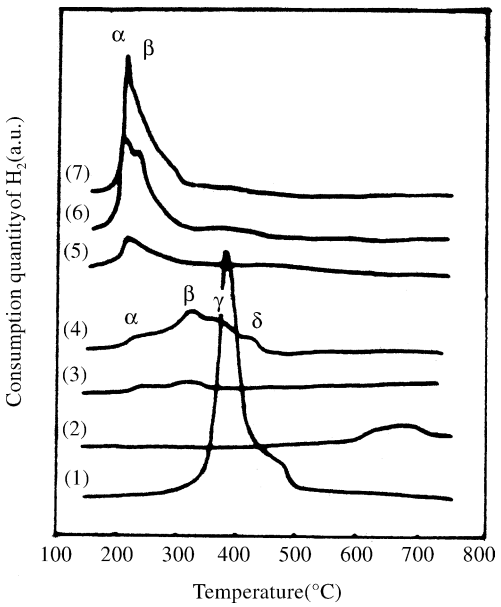

Fig. 6. TPR profiles of different catalysts. (1) CuO, (2) TiO_2, (3) 3% CuO/TiO_2, (4) 6% CuO/TiO_2, (5) 6% CuO-5% ZrO_2/TiO_2, (6) 6% CuO-10% ZrO_2/TiO_2, (7) 6% CuO-15% ZrO_2/TiO_2.

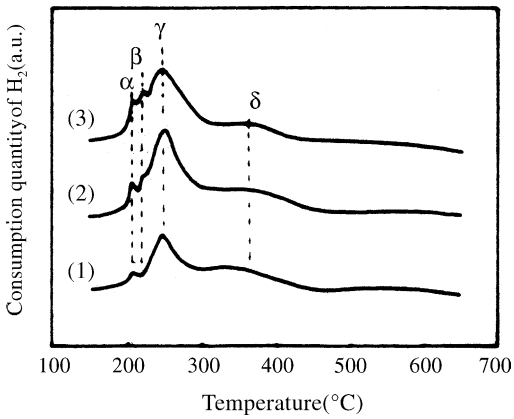

Fig. 7. TPR profiles of all catalysts calcined at 750 °C. (1) 6% CuO-5% ZrO_2/TiO_2, (2) 6% CuO-10% ZrO_2/TiO_2, (3) 6% CuO-15% ZrO_2/TiO_2.

observed at 392 and 650 °C for pure CuO and TiO_2, respectively, indicating that TiO_2 reduction was very difficult. In CuO/TiO_2, there were two reduction peaks (α, β) at 3% CuO loading compared with four reduction peaks (α, β, γ and δ) at 230, 325, 370 and 445 °C, respectively, when the amount of CuO loading was 6%. It was likely that the α peak resulted from the interaction of highly dispersed CuO species with TiO_2, and the β peak from the oxide clusters with a structure similar to CuO, i.e. short-range order but not crystallites. The γ peak could be due to the CuO crystallites, and the δ peak due to the interactions between CuO and TiO_2, and oxygen reduction on the TiO_2 surface [9,10].

After the addition of ZrO_2 into 6% CuO/TiO_2, the shape and area of TPR reduction peaks increased with increase in ZiO_2. Two reduction peaks (α and β) occurred in the TPR profile of 6% CuO-5% ZrO_2/TiO_2, with the β peak being pretty weak. When 10% ZrO_2 was added, both α and β peaks increased, whereas β peak disappeared at 15% ZrO_2 (Fig. 7). The results indicated that ZrO_2 might largely promote CuO dispersion on TiO_2. Therefore, the cause of improvement in catalytic activities was probably related to high dispersion of

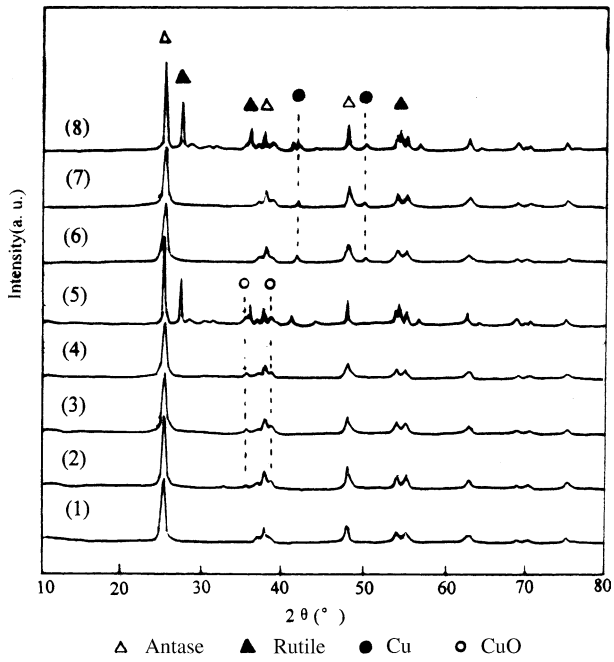

Fig. 8. XRD patterns of catalysts. (1) TiO_2, (2) 6% CuO/TiO_2, (3) 6% CuO-5% ZrO_2/TiO_2, (4) 6% CuO-15% ZrO_2/TiO_2, (5) 6% CuO-15% ZrO_2/TiO_2(750 °C), (6) 6% CuO/TiO_2 (500 °C, H_2 atmosphere), (7) 6% CuO-10% ZrO_2/TiO_2 (500 °C, H_2 atmosphere), (8) 6% CuO-15% ZrO_2/TiO_2 (750 °C, H_2 atmosphere).

CuO species (α peak) and fine grain CuO species (β peak). The XRD analysis also showed that addition of ZrO_2 into 6% CuO/TiO_2 did not increase the diffraction peak intensity of CuO (Fig. 8). When ZrO_2 loading increased to 15%, the diffraction peaks intensity of CuO remained unchanged, suggesting that highly dispersion CuO species and fine grain CuO species were the active center of NO reduction.

Fig. 7 shows the TPR profiles of CuO-ZrO_2/TiO_2 catalysts calcined at 750 °C. There were four reduction peaks (α, β, γ and δ) in lines (1)–(3) where the ZrO_2 loading ranged from 5 to 15%. At 5% ZrO_2 loading, the δ peak was smooth and the β peak not obvious. When the amount of

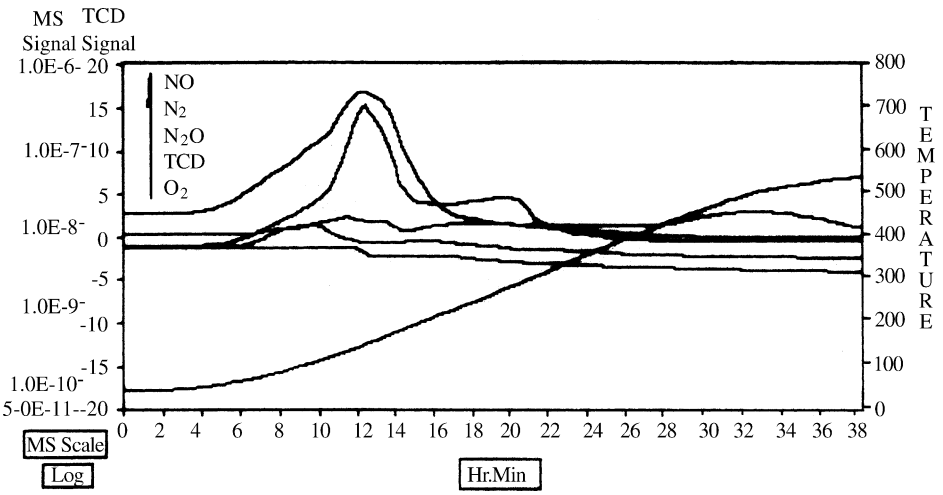

Fig. 9. NO-TPD spectra of 6% CuO/TiO_2 catalyst (air atmosphere) NO ($m/e = 30$), N_2O ($m/e = 44$), N_2 ($m/e = 28$), O_2 ($m/e = 32$).

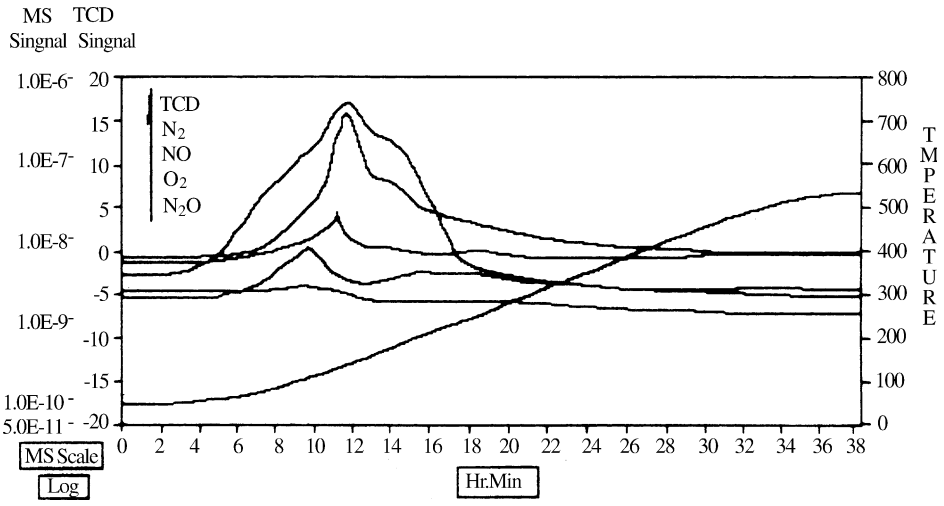

Fig. 10. NO-TPD spectra of 6% CuO-10% ZrO_2/TiO_2 catalyst (air atmosphere) NO ($m/e = 30$), N_2O ($m/e = 44$), N_2 ($m/e = 28$), O_2 ($m/e = 32$).

ZrO_2 loading was 10%, the β peak increased and the α peak had small changes. With further increase in ZrO_2 loading, the β peak intensity became weaker and the shape of TPR reduction peak smoother, suggesting that the catalysts calcined at 750 °C have the same TPR profiles as those calcined at normal temperature (500 °C).

3.6. XRD analysis of catalysts

As shown in line (1) of Fig. 8, there was a diffraction peak of anatase at 2θ; 25.2, 37.0 and 48.1° but not a rutile phase after TiO_2 was calcined at 450 °C for 4 h. Two CuO diffraction peaks were obvious between 2θ, 35.5 and 38.7° plus a diffraction peak of anatase phase (line 2), indicating that the CuO on TiO_2 had transformed from highly dispersion CuO species to a CuO crystal phase. After addition of ZrO_2 (5–15%), the diffraction peak of ZrO_2 was not detected (lines 3 and 4) and the diffraction peak intensity of CuO did not increase either. Likely, it was the strong interaction between CuO and ZrO_2 that enhanced the activity and stability of catalyst. XRD also detected a mixture phase of anatase and rutile after the catalysts were calcined at 750 °C for 2 h (line 5).

After 6% CuO/TiO_2 and 6% CuO-10% ZrO_2/TiO_2 were pretreated at 500 °C for 1 h in H_2, the CuO diffraction peaks ($d = 2.52$ and 2.33) disappeared but Cu diffraction peaks ($d = 2.09$ and 1.80) were detected, as shown in lines (6)–(8). By comparison, the catalysts calcined at 750 °C for 2 h in both H_2 and air atmospheres, the diffraction peaks of rutile ($d = 3.25$, 2.48 and 1.68) became much stronger additional to the conversion of CuO to Cu. The results indicate that the components changed and a strong interaction took place between the CuO and ZrO_2–TiO_2 compounds. Based on the results of this study and a previous study by Yasuaki et al. [12], we suggest that in H_2 atmosphere CuO produced dispersed Cu^0 species, and after one NO molecule on the Cu^0 sites formed a mononitrosyl Cu^0 species, another NO molecule reacted with the mononitrosyl Cu^0 species to pro-

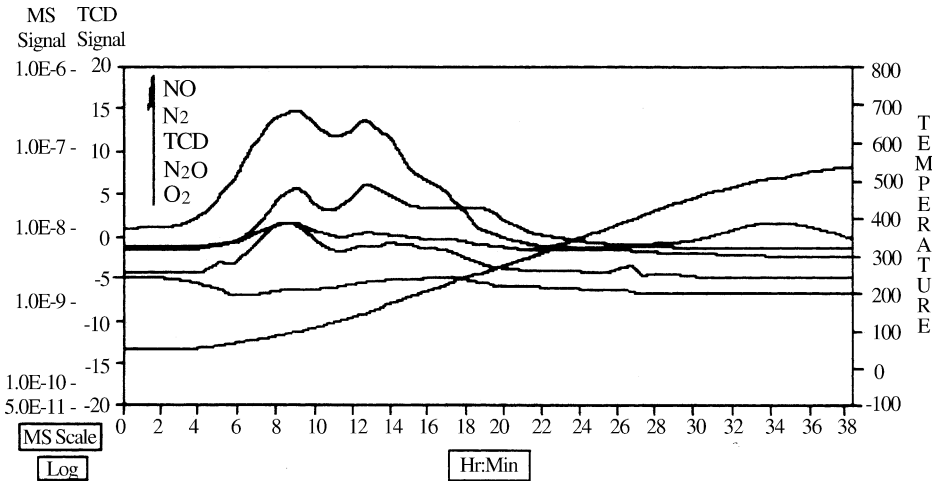

Fig. 11. NO-TPD spectra of 6% CuO/TiO_2 catalyst (H_2 atmosphere) NO ($m/e = 30$), N_2O ($m/e = 44$), N_2 ($m/e = 28$), O_2 ($m/e = 32$).

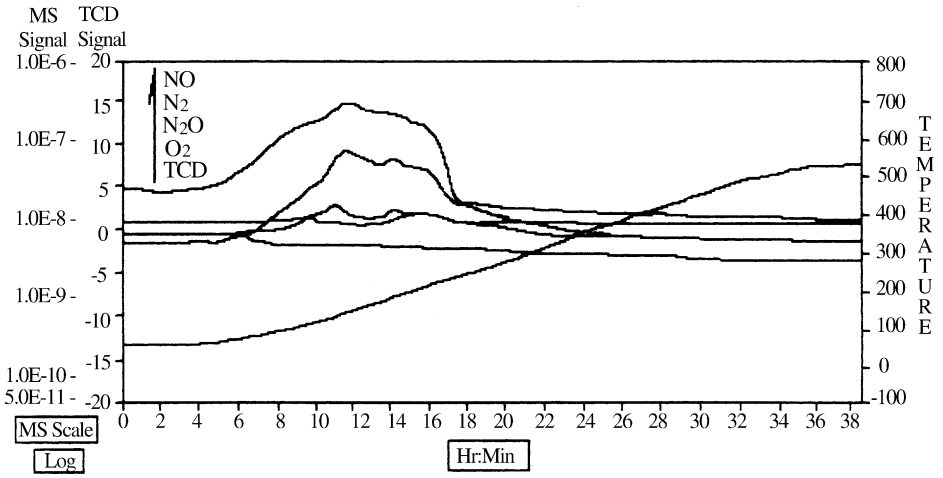

Fig. 12. NO-TPD spectra of 6% CuO-10% ZrO_2/TiO_2 catalyst (H_2 atmosphere) NO ($m/e = 30$), N_2O ($m/e = 44$), N_2 ($m/e = 28$), O_2 ($m/e = 32$).

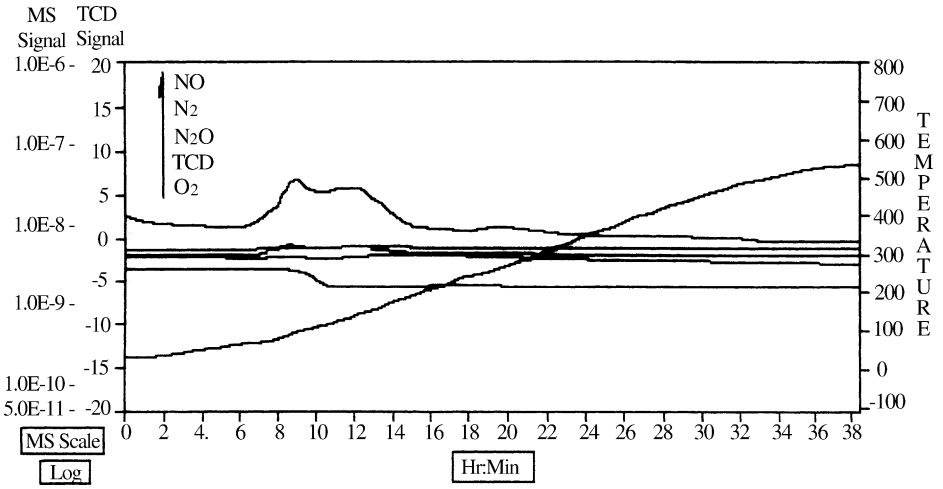

Fig. 13. NO-TPD spectra of 6% CuO/TiO_2 catalyst (750 °C, H_2 atmosphere) NO ($m/e = 30$), N_2O ($m/e = 44$), N_2 ($m/e = 28$), O_2 ($m/e = 32$).

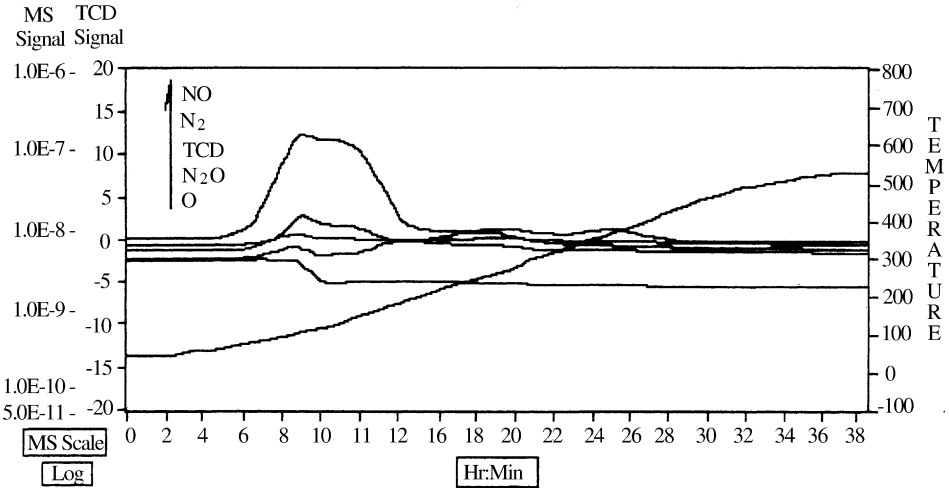

Fig. 14. NO-TPD spectra of 6% CuO-10% ZrO_2/TiO_2 catalyst (750 °C, H_2 atmosphere) NO ($m/e = 30$), N_2O ($m/e = 44$), N_2 ($m/e = 28$), O_2 ($m/e = 32$).

duce N_2O and an unstable dinitrosyl intermediate, and then returned back to Cu^0 species, i.e. a continuous redox cycle involving Cu^{2+} and Cu^0. It was likely that NO reacted with a mononitrosyl Cu^0 species to form N_2 and dispersed Cu^0 species.

3.7. NO-TPD experiment

After the surface of 6% CuO/TiO_2 adsorbed NO, thermal desorption took place as a dissociation reaction, and four desorption species (NO, $m/e = 30$; N_2O, $m/e = 44$; N_2, $m/e = 28$ and O_2, $m/e = 32$) (Fig. 9) were detected by mass spectrometer. The NO desorption of 6% CuO/TiO_2 and 6% CuO-10% ZrO_2/TiO_2 pretreated in air atmosphere had three and four desorption peaks, respectively, i.e. three and four NO adsorption centers, and desorption peak temperatures were 100, 160, 200 °C, and 80, 110, 140, 180 °C, respectively. When the catalysts were pretreated in H_2, their NO desorption also had three desorption peaks, one peak due to NO adsorption on weak sites and the other two peaks due to NO adsorption on strong sites, and desorption peak temperature were 100, 150 and 220 °C, respectively. After 10% ZrO_2 was added into 6% CuO/TiO_2, four NO desorption peaks occurred at 60, 100, 150 and 180 °C, indicating that NO desorption by CuO-ZrO_2/TiO_2 was easier than that by CuO/TiO_2. In addition, desorption peak temperature of NO by 6% CuO-10% ZrO_2/TiO_2 was lower than that by 6% CuO/TiO_2, i.e. the former catalyst had higher NO dissociation activity than the latter catalyst. The two catalysts also showed N_2O desorption peak at low temperatures but N_2 desorption peak at high temperatures. The NO-TPD process detected NO but not O_2 desorption peak. It was likely that NO dissociation produced atomic oxygen (O) that dispersed or entered into the bulk of Cu [13,14], and the desorption of atomic oxygen could only occur at high temperatures (Figs. 10–14).

4. Conclusion

(1) The activities of CuO/TiO_2 catalysts pre-treated in H_2 were much higher than those pre-treated in air at 500 °C for 1 h. The temperatures ($T_{99\%}$) of NO conversion were 325 °C in H_2 and 450 °C in air. After ZrO_2 was added into CuO/TiO_2, the catalytic activities were similar to that of CuO/TiO_2 in both atmospheres, i.e. $T_{99\%}$ was 300 °C in H_2 and 350 °C in air.

(2) An addition of 5% ZrO_2 into CuO/TiO_2 calcined at 750 and 850 °C for 2 h caused small changes in anti-high temperature property, whereas 15% ZrO_2 addition significantly increased catalytic activities, thermal stability and N_2 selectivity in the NO + CO reaction.

(3) There were four reduction peaks (α, β, γ and δ) in CuO/TiO_2 but only two reduction peaks in CuO-ZrO_2/TiO_2 at 6% CuO loading. After addition of ZrO_2 into CuO/TiO_2, some change in TPR reduction peaks took place.

(4) The catalysts pre-treated in air displayed CuO diffraction peaks, whereas those pre-treated in H_2 displayed Cu diffraction peaks.

(5) Four desorption species (NO, N_2O, N_2 and O_2) were produced during the thermal desorption of NO adsorbed on CuO/TiO_2 and CuO-ZrO_2/TiO_2. The desorption species at low temperature were the NO adsorption on weak sites and those at high temperature on strong sites. Addition of ZrO_2 into CuO/TiO_2 shifted the NO desorption peaks towards the low temperature range, i.e. the NO dissociation activity by CuO-ZrO_2/TiO_2 was higher than that by CuO/TiO_2.

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