

# Preparation, characterization and activity of novel silica-pillared layered titanoniobate supported copper catalysts for the direct decomposition of NO

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## Abstract

A series of silica-pillared layered titanoniobate supported copper catalysts (Cu/Si-TiNbO<sub>5</sub>) were prepared for the direct decomposition of NO. It was found that Cu/Si-TiNbO<sub>5</sub> catalysts were highly active for the reaction of NO (0.1 vol.% in He) decomposition in the space velocity range of 3000–30,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>. The 3.5 wt.% Cu/Si-TiNbO<sub>5</sub> catalyst showed the highest conversion into N<sub>2</sub> for NO decomposition. While 2.0 wt.% Cu/Si-TiNbO<sub>5</sub> had the highest specific activity at low temperature ( $\leq 550^\circ\text{C}$ ) and 1.0 wt.% Cu/Si-TiNbO<sub>5</sub> showed the highest specific activity at high temperature ( $> 550^\circ\text{C}$ ). XRD and temperature-programmed reduction (TPR) results indicated that there existed well-dispersed copper oxide species and large copper oxide particles in the catalysts. Well-dispersed copper oxide species were reduced more easily than large copper oxide particles by H<sub>2</sub>. X-ray photoelectron spectra (XPS) and Auger electron spectra (AES) results revealed that Cu<sup>+</sup> species existed in Cu/Si-TiNbO<sub>5</sub> catalysts and that the copper oxide species in Cu/Si-TiNbO<sub>5</sub> catalysts after used for NO decomposition were different from those before the reaction. Well-dispersed copper oxide species were active for NO decomposition and the most active sites might be the dimeric copper oxide species over the support. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** NO decomposition; Copper oxide; Layered titanoniobate; Pillaring; Silica

## 1. Introduction

Air pollution induced by nitrogen oxide (NO<sub>x</sub>) in the exhaust gases from automobiles and power plants has become a serious problem. Atmospheric emissions of NO<sub>x</sub> not only have detrimental effect on human health, but also have adverse effects on ecosystems in which we live. Therefore, the development of excellent catalysts to remove NO<sub>x</sub> is of great importance. Since nitrogen monoxide (NO) is thermodynamically unstable relative to N<sub>2</sub> and O<sub>2</sub> at lower

temperature [1], the direct decomposition of NO into its elements over a solid catalyst is considered to be one of the main catalytic approaches to the elimination of nitrogen monoxide from the exhaust gases. To date, many catalysts, such as noble metals [2–8], mixed metal oxides [9–16] and metal ion-exchanged molecular sieves [17–26] have already been investigated extensively. Among them, Cu ion-exchanged ZSM-5 is the only catalyst showing sufficiently high and stable activity for NO decomposition. To develop new catalysts which have high activity and stability is of great significance.

Metal oxides pillared layered materials are two-dimensional zeolite-like materials. They are usually prepared by intercalating large inorganic hydroxycations,

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which are polymeric or oligomeric hydroxy metal cations formed by the hydrolysis of metal oxides or salts. Upon heating, the metal hydroxy cations undergo dehydration and dehydroxylation, forming stable metal oxide clusters which act as pillars keeping the matrix layers separated, creating interlayer space of molecular dimensions. Since these materials have a number of attractive features, such as high porosity, high surface area and high thermal stability, they have attracted considerable attention as catalysts and adsorbents. In particular, smectite clays pillared by metal oxides have been successfully used as dehydrogenation and selective oxidation catalysts [27–29] and as acid catalysts in several organic reactions [30]. Ion-exchange pillared clays also have been found to be active for the selective catalytic reduction of NO by  $\text{NH}_3$  or hydrocarbons [31–34]. On the other hand, pillared derivatives of some layered phosphates [35,36], titanates [37], lanthanum-niobates [38] and titanoniobates [39] have also been prepared, but their applications in catalysis have hardly been investigated. Silica-pillared layered titanoniobate prepared by the reaction of  $\text{HTiNbO}_5$  powder with an aqueous solution of  $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ , is a new porous material with high specific surface area, thermal stability ( $>700^\circ\text{C}$ ) and medium acidic strength. It could be an ideal support of catalysts. In this paper, using silica-pillared layered titanoniobate as support, a novel series of Cu catalysts were first prepared for the direct decomposition of NO, and it was found that these catalysts had relatively high and stable activity for the direct decomposition of NO. The catalysts were characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), X-ray photoelectron spectra (XPS) and Brunauer–Emmett–Teller (BET) surface area measurement.

## 2. Experimental

### 2.1. Synthesis of silica-pillared layered titanoniobate and preparation of catalysts

$\text{KTiNbO}_5$  was prepared by solid-state reaction of an intimate mixture of  $\text{K}_2\text{CO}_3$ ,  $\text{TiO}_2$  and  $\text{Nb}_2\text{O}_5$  in the molar ratio of 1:2:1 at  $1100^\circ\text{C}$  for 24 h according to Hou et al. [40].  $\text{HTiNbO}_5$  was obtained by a two-step cation-exchange reaction. Then 15 g  $\text{KTiNbO}_5$  pow-

der was added to 900 ml of 2 M HCl solution under stirring at  $60^\circ\text{C}$  for 2 h, followed by centrifugation and washed with distilled water twice. The obtained solid product was added to 900 ml of freshly prepared 2 M HCl solution again under the same condition for 2 h, so that  $\text{K}^+$  could be completely exchanged by  $\text{H}^+$ . The final product was fully washed with distilled water until the liquid phase is free of chloride ions by silver nitrate test, and then dried at  $50^\circ\text{C}$  for 24 h.

Silica-pillared layered titanoniobate (represented by  $\text{Si-TiNbO}_5$ ) was prepared by adding  $\text{HTiNbO}_5$  powder, under stirring, to a freshly prepared 10 wt.% aqueous solution of  $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$  ( $\text{Si}:\text{Ti} = 10:1$ ). The dispersion was refluxed for 60 h, followed by centrifugation and fully washed with distilled water, then air-dried at  $50^\circ\text{C}$  for 24 h and calcined in air at  $500^\circ\text{C}$  for 12 h. After calcined in air at  $700^\circ\text{C}$ , the sample still showed obvious (0 0 2) ( $2\theta = 8.2^\circ$ ) reflection peak, characteristic of crystalline layered structures, indicating the material had a high thermal stability.

Silica-pillared layered titanoniobate supported Cu catalysts (represented by  $\text{Cu/Si-TiNbO}_5$ ) were prepared by impregnation of  $\text{Si-TiNbO}_5$  powder with aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$ . Then 2 g of  $\text{Si-TiNbO}_5$  powder was soaked into 4 ml corresponding aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$  under stirring at room temperature for 1.5 h, then evaporated at  $60^\circ\text{C}$  for 2 h, dried at  $100^\circ\text{C}$  overnight, and finally calcined at  $500^\circ\text{C}$  in air for 3 h. The copper loadings of  $\text{Cu/Si-TiNbO}_5$  samples prepared were 1.0, 2.0, 3.5, 5.0 and 6.5 wt.%, respectively.

### 2.2. Characterization

XRD patterns were obtained on a Shimadzu XD-3A diffractometer operating with Cu  $\text{K}\alpha$  radiation and a Ni filter. The BET surface area and  $\text{N}_2$  adsorption–desorption isotherm of the samples were measured volumetrically at liquid-nitrogen temperature on a Micromeritics ASAP-2000 instrument. The samples were evacuated at  $200^\circ\text{C}$  to reach a vacuum below 3  $\mu\text{mHg}$  before the measurements being made.

XPS and Auger electron spectra (AES) were recorded with an ESCALAB MK-II spectrometer equipped with an Mg  $\text{K}\alpha$  X-ray excitation source. The C 1s peak at 284.6 eV was used as the reference for binding energies.

TPR experiments were carried out in a home-built device. Prior to the measurements, the samples were calcined in air at 500°C for 2 h. After cooling, a 15% H<sub>2</sub>/Ar flow of 30 ml min<sup>-1</sup> was passed through a quartz reactor containing 100 mg of the sample (10 mg CuO for comparison). The temperature was increased from 50 to 650°C at a heating rate of 10°C min<sup>-1</sup>.

### 2.3. Catalytic activity measurement

The catalytic decomposition of NO was carried out in a fixed-bed flow reactor at atmospheric pressure. A quartz glass tube (4 mm i.d.) was used as a reactor, and the temperature was monitored by a chromel–alumel thermocouple. Then 0.1 g of catalyst was placed in the reactor and supported by quartz wool. The reactant gas was 0.1 vol.% NO in He. The flow rate was controlled by rotameter. Prior to the reaction, the catalysts were pretreated in a flow of He at 500°C for 2 h in order to remove the impurities on the catalyst surface, then cooled to 100°C in a He stream and the reactant gas was introduced. The reaction temperature was increased stepwise in 50 or 100 intervals from 100 to 750°C. After the reaction was carried out at each temperature for 30 min, the products were analyzed on-line by a gas chromatograph (FULI GC 9790) at 50°C with a 5 Å molecular sieve column for N<sub>2</sub> and O<sub>2</sub>, and Porapak Q column for N<sub>2</sub>O.

## 3. Results

### 3.1. BET measurement

The N<sub>2</sub> adsorption isotherm of the silica-pillared layered titanoniobate calcined in air at 500°C for 12 h was of type IV in the classification of Brunauer–Deming–Deming–Teller (BDDT), indicating the presence of both microporous and mesoporous. The N<sub>2</sub> adsorption–desorption isotherm of the sample showed an apparent hysteresis loop of H3 type as classified by Sing et al. [41], suggesting that

the material possessed a porous structure associated with aggregates of plate-like particles giving rise to slit-shape pores. Table 1 gives some physical parameters of Si-TiNbO<sub>5</sub>. It can be seen that the sample has a high specific surface area and a pore volume with an average diameter of 26.7 Å. On the contrary, the starting material KTiNbO<sub>5</sub> is nonporous, with a very low BET surface area of 1.8 m<sup>2</sup> g<sup>-1</sup>. The large microporous surface area (82.3 m<sup>2</sup> g<sup>-1</sup>) also confirmed the successful insertion of silica pillars between the titanoniobate layers.

### 3.2. XRD measurement

XRD patterns of Si-TiNbO<sub>5</sub> and Cu/Si-TiNbO<sub>5</sub> are shown in Fig. 1. All these samples showed a basal reflection (0 0 2) and two-dimensional reflections, which is characteristic of evident crystalline layered structures. This indicates that the samples with different Cu loadings still retain original layered structures. For all the samples, the 2θ angle of the (0 0 2) reflection was 8.1 ± 0.1°, which corresponded to a *d*-spacing of 10.5 Å, showing the interlayer distance of the support did not change after the impregnation

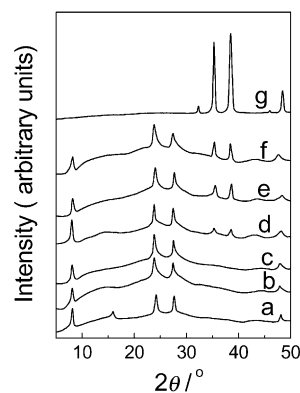


Fig. 1. XRD patterns of Cu/Si-TiNbO<sub>5</sub> catalysts with different Cu loadings: (a) 0 wt.%; (b) 1.0 wt.%; (c) 2.0 wt.%; (d) 3.5 wt.%; (e) 5.0 wt.%; (f) 6.5 wt.% and (g) CuO.

Table 1

Some physical parameters of silica-pillared layered titanoniobate calcined in air at 500°C for 12 h

| Interlayer distance (Å) | Pillaring height (Å) | Average pore diameter (Å) | Surface area (BET, m <sup>2</sup> g <sup>-1</sup> ) | Microporous area (m <sup>2</sup> g <sup>-1</sup> ) | Porous volume (ml g <sup>-1</sup> ) |
|-------------------------|----------------------|---------------------------|-----------------------------------------------------|----------------------------------------------------|-------------------------------------|
| 10.9                    | 4.8                  | 26.7                      | 132.3                                               | 82.3                                               | 0.12                                |

of copper nitrate solution. For 1.0 and 2.0 wt.% Cu/Si-TiNbO<sub>5</sub> catalysts, their XRD patterns were similar to that of the support Si-TiNbO<sub>5</sub> and no peak for copper oxide was observed, suggesting that CuO was dispersed well on the support. For 3.5 wt.% Cu/Si-TiNbO<sub>5</sub>, two small peaks were detected at  $2\theta = 35.6$  and  $38.8^\circ$ , which are attributed to the diffraction of crystalline CuO (Fig. 1d and g). The intensities of these two peaks gradually increased with the increase of Cu loading (Fig. 1e and f).

### 3.3. Decomposition of NO on Cu/Si-TiNbO<sub>5</sub>

NO direct decomposition over a series of Cu/Si-TiNbO<sub>5</sub> catalysts with different Cu loadings was studied in the temperature range from 100 to 700°C at the space velocity of 6000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup> and the results are shown in Fig. 2. The space velocity was defined as the total flow rate over the weight of catalyst. It could be found that all the Cu/Si-TiNbO<sub>5</sub> catalysts had obviously catalytic activity, while the catalytic activity of Si-TiNbO<sub>5</sub> was very low. This indicated that the loaded copper was the active component in this reaction. The conversion of NO decomposition into N<sub>2</sub> increased with the Cu loading up to 3.5 wt.%, and then began to decrease with the further increase of Cu loading. The 3.5 wt.% Cu/Si-TiNbO<sub>5</sub> catalyst showed the highest NO conversion into N<sub>2</sub>. For the Cu loading beyond 3.5 wt.%, a maximum conversion appeared around 620–670°C. In Fig. 2, it could also be seen that 5.0 wt.% Cu/Si-TiNbO<sub>5</sub> had the highest NO conversion into O<sub>2</sub>. For all the catalysts, the amounts of NO conversion into N<sub>2</sub> and O<sub>2</sub> were not equal. The discrepancy between them may be attributed to the reaction of NO<sub>2</sub> formation, in which part of O<sub>2</sub> generated by the NO decomposition will further react with undecomposed NO.

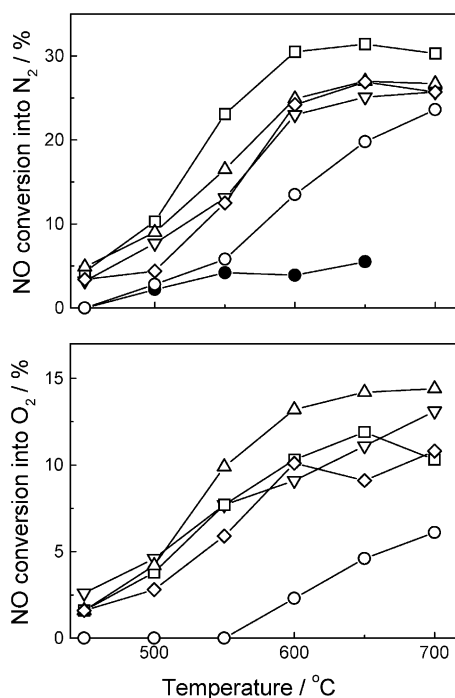


Fig. 2. Effect of temperature on the conversion of NO decomposition into N<sub>2</sub> and O<sub>2</sub> over Cu/Si-TiNbO<sub>5</sub> catalysts (SV = 6000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>): (●) 0 wt.% Cu/Si-TiNbO<sub>5</sub>; (○) 1.0 wt.% Cu/Si-TiNbO<sub>5</sub>; (▽) 2.0 wt.% Cu/Si-TiNbO<sub>5</sub>; (□) 3.5 wt.% Cu/Si-TiNbO<sub>5</sub>; (△) 5.0 wt.% Cu/Si-TiNbO<sub>5</sub> and (◇) 6.5 wt.% Cu/Si-TiNbO<sub>5</sub>.

Table 2 gives the apparent turnover frequencies (ATOF, expressed as moles of NO converted to N<sub>2</sub> per mole of Cu per second) for NO converted to N<sub>2</sub> over Cu/Si-TiNbO<sub>5</sub> catalysts at different temperatures. When the reaction temperature was low ( $\leq 550^\circ\text{C}$ ), the ATOF first increased with Cu loading and reached the maximum at 2.0 wt.% Cu loading, then decreased

Table 2

Dependence of ATOFs on Cu loadings and reaction temperatures (SV = 6000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>)

| Samples                           | ATOF ( $\times 10^4 \text{ s}^{-1}$ ) |       |       |       |       |       |
|-----------------------------------|---------------------------------------|-------|-------|-------|-------|-------|
|                                   | 450°C                                 | 500°C | 550°C | 600°C | 650°C | 700°C |
| 1.0 wt.% Cu/Si-TiNbO <sub>5</sub> | 0.0                                   | 17.7  | 36.2  | 84.2  | 123.6 | 147.3 |
| 2.0 wt.% Cu/Si-TiNbO <sub>5</sub> | 10.0                                  | 24.1  | 40.9  | 71.9  | 78.4  | 80.3  |
| 3.5 wt.% Cu/Si-TiNbO <sub>5</sub> | 7.7                                   | 18.4  | 41.3  | 54.6  | 56.2  | 54.2  |
| 5.0 wt.% Cu/Si-TiNbO <sub>5</sub> | 6.1                                   | 9.0   | 20.7  | 31.2  | 33.8  | 33.5  |
| 6.5 wt.% Cu/Si-TiNbO <sub>5</sub> | 3.3                                   | 4.2   | 12.0  | 23.3  | 25.9  | 24.7  |

with the further increase of Cu loading. For 1.0 wt.% Cu/Si-TiNbO<sub>5</sub>, when the reaction temperature was higher above 550°C, the ATOF increased drastically with the reaction temperature and became much higher than those of the others. It can be seen that 2.0 wt.% Cu/Si-TiNbO<sub>5</sub> at low temperatures (450, 500 and 550°C) and 1.0 wt.% Cu/Si-TiNbO<sub>5</sub> catalyst at high temperatures (600, 650 and 700°C) have the highest ATOFs, respectively, although 3.5 wt.% Cu/Si-TiNbO<sub>5</sub> had the highest NO conversion into N<sub>2</sub> for NO decomposition.

In addition, among the products of the NO decomposition over each Cu/Si-TiNbO<sub>5</sub> catalyst in the temperature range from 100 to 700°C, N<sub>2</sub>O, which is more harmful than CO<sub>2</sub> as a green house effect gas, was not detected.

#### 3.4. Dependence of the catalytic activity on space velocity and on the reaction time

From a practical point of view, the activity at high space velocity is very important. As an example, the dependences of the catalytic activities over 3.5 wt.% Cu/Si-TiNbO<sub>5</sub> on space velocity (SV) are shown in Fig. 3. With the increase of SV, the conversion of NO into N<sub>2</sub> gradually decreased. Under low space velocities, the conversions of NO decomposition into N<sub>2</sub> appeared a maximum. With further increasing the space

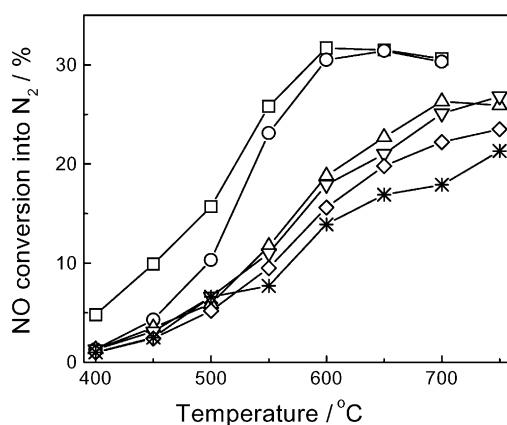


Fig. 3. Dependency of the conversion of NO decomposition over 3.5 wt.% Cu/Si-TiNbO<sub>5</sub> on space velocity: (□) 3000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>; (○) 6000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>; (△) 12,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>; (▽) 18,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>; (◇) 24,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup> and (\*) 30,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>.

Table 3

Conversion of NO direct decomposition into N<sub>2</sub> and O<sub>2</sub> over 3.5 wt.% Cu/Si-TiNbO<sub>5</sub> under different space velocities at 650°C

| Space velocity<br>(cm <sup>3</sup> g <sup>-1</sup> h <sup>-1</sup> ) | Conversion of<br>NO to N <sub>2</sub> (%) | Conversion of<br>NO to O <sub>2</sub> (%) |
|----------------------------------------------------------------------|-------------------------------------------|-------------------------------------------|
| 3000                                                                 | 31.5                                      | 12.5                                      |
| 6000                                                                 | 31.4                                      | 10.3                                      |
| 12000                                                                | 22.7                                      | 8.8                                       |
| 18000                                                                | 21.0                                      | 9.4                                       |
| 24000                                                                | 19.8                                      | 9.5                                       |
| 30000                                                                | 16.9                                      | 10.9                                      |

velocity, the temperature corresponding to the maximum conversion shifted to higher position. When the space velocity increased up to 18,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>, no maximum appeared. It can be seen in Table 3 that the conversion of NO into O<sub>2</sub> did not have a noticeable change, although the conversion into N<sub>2</sub> decreased gradually with increasing the space velocity. This indicates that the formations of N<sub>2</sub> and O<sub>2</sub> may proceed through separate rate-limiting steps.

The variation of the NO decomposition over 3.5 wt.% Cu/Si-TiNbO<sub>5</sub> with the reaction time at 650°C is shown in Fig. 4. It can be seen that the NO conversion into N<sub>2</sub> decreases with increasing the reaction time from 0 to 20 h, while that into O<sub>2</sub> increases gradually with increasing the reaction time. It reveals that the formation of NO<sub>2</sub> from the reaction of undecomposed NO with O<sub>2</sub>, generated by the decomposition of NO, are mainly catalyzed by copper

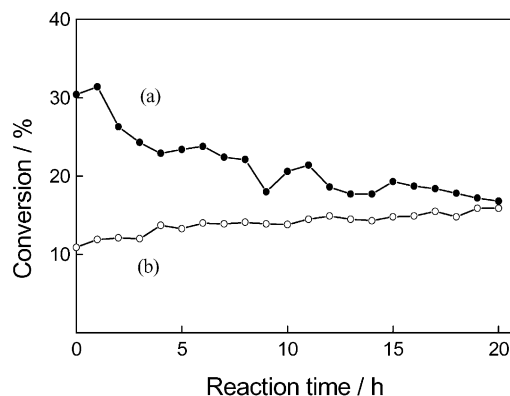


Fig. 4. Dependence of the conversion of NO decomposition into N<sub>2</sub> (a), and O<sub>2</sub> (b) with reaction time over 3.5 wt.% Cu/Si-TiNbO<sub>5</sub> catalyst at 650°C (SV = 6000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>).

species and the homogeneous oxidation is negligible, and this catalytic oxidation reaction gradually deactivated with the reaction time.

### 3.5. $H_2$ -TPR study

Since the reduction behavior of the dispersed metal ions is usually different from that of the corresponding bulk metal oxide, TPR can be used to characterize the dispersion of metal ions in catalyst prepared via different routes. The reduction profile provides information on the dispersion of the metal species over the support and on the interaction between the metal ions and the support [42]. The TPR profiles for all the Cu/Si-TiNbO<sub>5</sub> catalysts are showed in Fig. 5, along with the TPR profile of unsupported CuO for comparison. It can be seen that all Si-TiNbO<sub>5</sub> supported copper oxides exhibited different reduction behavior from unsupported bulk copper oxide and the catalysts with different Cu loadings showed different types of  $H_2$  reduction peaks. This indicated that there existed different copper species and these species were different from unsupported bulk copper oxide. For 1.0 wt.% Cu/Si-TiNbO<sub>5</sub> catalyst, a small broad peak with reduction occurring continuously between ca. 165 and 430°C compared to the support was observed (Fig. 5b and c), and the maximum temperature was unresolved. This may be ascribed to the reduction of isolated Cu ions and very fine CuO particles dispersed over the support surface. Isolated copper ions can be reduced

to Cu<sup>0</sup> by  $H_2$  in two steps:  $Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0$ ; while CuO particles was reduced directly to Cu<sup>0</sup> in one step:  $CuO \rightarrow Cu^0$  [34]. Therefore, the peak may include the reduction of two copper species: that of isolated Cu ions and that of very small dispersed CuO particles. In Fig. 5d, a main peak at 245°C appeared and a tail from 305 to 430°C could also be seen with 2.0 wt.% Cu/Si-TiNbO<sub>5</sub> catalyst. This may also be assigned to the small CuO particles well dispersed on the support and isolated Cu ions. As Cu loading increased up to 3.5 wt.%, two obvious resolved reduction peaks appeared, suggesting that there existed two copper species, while unsupported CuO only had a very narrow peak centered at 277°C. In addition, the tail from 305 to 430°C, which can be observed in the catalysts with lower Cu loadings, disappeared, indicating that there are mainly fine and bulk CuO particles, and no isolated Cu<sup>+</sup> in the catalysts with high Cu loadings. It can be seen in Fig. 5 that the position of the low-temperature reduction peak was independent of Cu loading for 3.5, 5.0 and 6.5 wt.% Cu/Si-TiNbO<sub>5</sub> catalysts, the low temperature  $H_2$  consumption peaks were located at 244, 244, and 245°C, respectively, which are the same as the main peak of 2.0 wt.% Cu/Si-TiNbO<sub>5</sub> catalysts, and more than 30°C lower than that of bulk CuO reduction. It may be concluded that the low-temperature reduction peaks arose from the reduction of very fine CuO particles well-dispersed on the Cu/Si-TiNbO<sub>5</sub> support. The ease of the reduction for the supported copper oxide, as compared to the bulk oxide, may be due to the interaction between the support and dispersed copper oxide particles, but it is also probably due to the higher dispersion, which provides a larger reactive surface area and, therefore, a high concentration of defects at which the reduction reaction can start [42,43]. It can also be seen in Fig. 5 that the amount of  $H_2$  consumption for the high-temperature reduction process increased with the increase of Cu loading. Together with XRD results, it can be concluded that the high temperature reduction peak is associated with the formation of the large crystalline CuO particles. With the increase of copper content, the size of the crystalline CuO particles formed on the support became larger and, therefore, the corresponding reduction peak shifted to higher temperature from 292°C for 3.5 wt.% Cu/Si-TiNbO<sub>5</sub> to 313°C for 6.5 wt.% Cu/Si-TiNbO<sub>5</sub> [44]. The reduction of the large crystalline CuO particles over Si-TiNbO<sub>5</sub> needed

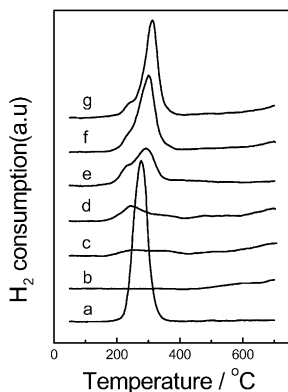


Fig. 5. TPR profiles of Cu/Si-TiNbO<sub>5</sub> catalysts and unsupported CuO: (a) unsupported CuO; (b) 0 wt.%; (c) 1.0 wt.%; (d) 2.0 wt.%; (e) 3.5 wt.%; (f) 5.0 wt.% and (g) 6.5 wt.%.

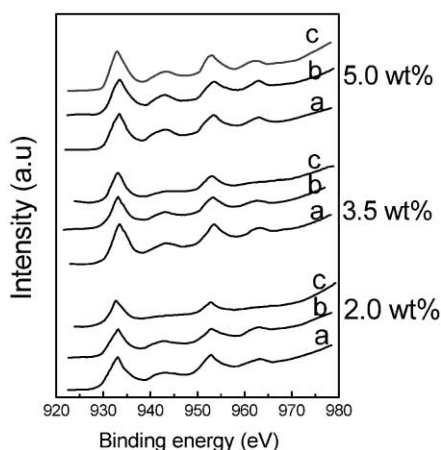


Fig. 6. XPS spectra of Cu  $2p_{3/2}$  band of (a) fresh, (b) treated in He at 500°C, and (c) used for NO decomposition.

higher temperature than that of unsupported bulk CuO. This is probably due to the effect of the porous structure of the support [45].

### 3.6. XPS and AES study

Fig. 6 gives Cu 2p XPS results of 2.0, 3.5, 5.0 wt.% Cu/Si-TiNbO<sub>5</sub> catalysts under different conditions and the binding energies of some Cu  $2p_{3/2}$  are summarized in Table 4. It can be seen that the intensity ratio of the satellite to the main peak increased with the Cu loading for fresh catalysts (treated at 500°C in air for 3 h) (Fig. 6a), and Cu  $2p_{3/2}$  binding energies gradually increased close to 933.6 eV, characteristic of CuO species, the corresponding Cu<sub>L3MM</sub> AES peaks are located at 917.6 eV. This shows that there might exist small amount of Cu<sup>+</sup> in the catalysts and Cu<sup>+</sup> frac-

tion diminished with the increase of Cu loading. The Cu 2p XPS spectra of 2.0, 3.5 and 5.0 wt.% catalysts after treated at 500°C in a flow of He for 3 h are also given in Fig. 6b for comparison. No obvious change was detected, indicating that the copper oxide species did not change on the surface of Si-TiNbO<sub>5</sub> support in He atmosphere. It is worth noting that Cu 2p XPS spectra of the catalysts after used in NO decomposition were obviously different from those of fresh catalysts. In each case, the Cu  $2p_{3/2}$  binding energies decreased after the catalysts being used. The satellite peaks, which is indicative of Cu(II) species, disappeared for the 2.0% Cu/Si-TiNbO<sub>5</sub> (Fig. 6c). For other catalysts used, the intensity of the satellite peak also obviously decreased (Fig. 6c). The AES results also showed that for all the used catalyst, there appeared new weak Cu<sub>L3MM</sub> peaks at 916.9 eV, characteristic of Cu<sup>+</sup> [46]. These results suggested a change in the copper environment and more Cu<sup>+</sup> species formed in the catalysts after used in NO decomposition.

## 4. Discussion

### 4.1. Copper oxide species over Si-TiNbO<sub>5</sub>

Silica-pillared layered titanoniobate was formed by intercalating silica pillars into the titanoniobate layers. Its surface area consisted of two parts: the surface area of silica pillars and that of titanoniobate layers. It is difficult to identify whether Cu species are on the pillars or on the layers. However, from the XRD and TPR results, it can be concluded that there are both well-dispersed Cu oxide species and large CuO particles in the catalysts. These two kinds of Cu oxide species are different. Well-dispersed Cu species could be reduced more easily than large CuO particles. Since the low temperature reduction processes were almost unaffected with the Cu loading, we supposed that well-dispersed Cu species and large CuO particles might be located at different sites. XPS results indicated that part of Cu<sup>+</sup> existed in Cu/Si-TiNbO<sub>5</sub> catalysts and the ratio of Cu<sup>+</sup>/Cu<sup>2+</sup> decreased with the Cu loading. As shown in Fig. 6, the Cu 2p XPS spectra of Cu/Si-TiNbO<sub>5</sub> catalyst treated in He were the same as that of fresh catalysts, indicating Cu species did not change. However, after used in NO decomposition reaction, the Cu 2p XPS spectra showed that

Table 4  
Cu  $2p_{3/2}$  XPS results of Cu/Si-TiNbO<sub>5</sub> catalysts

| Samples                           | Cu $2p_{3/2}$ (eV) |               |                |
|-----------------------------------|--------------------|---------------|----------------|
|                                   | Fresh              | Treated in He | After reaction |
| 1.0 wt.% Cu/Si-TiNbO <sub>5</sub> | 933.1              |               |                |
| 2.0 wt.% Cu/Si-TiNbO <sub>5</sub> | 933.2              | 933.4         | 932.6          |
| 3.5 wt.% Cu/Si-TiNbO <sub>5</sub> | 933.2              | 933.2         | 932.7          |
| 5.0 wt.% Cu/Si-TiNbO <sub>5</sub> | 933.5              | 933.8         | 933.1          |
| 6.5 wt.% Cu/Si-TiNbO <sub>5</sub> | 933.6              |               |                |

more  $\text{Cu}^{2+}$  were reduced to  $\text{Cu}^+$ . This may be caused by the desorption of part of oxygen atoms on the surface of the catalysts during the reaction. At present, the real reason is still not clear, and further research work is needed.

#### 4.2. Decomposition of NO

The reaction mechanism of NO decomposition on Cu-ZSM-5 has been extensively investigated [47–49]. It was reported that only the copper species close to the support were active in the NO decomposition. The most active copper sites might be the dimeric ones  $(\text{Cu}^{2+}-\text{O}-\text{Cu}^{2+})^{2+}$ , which are the reactive sites for  $\text{Cu}^+$  formation. These species, under steady state conditions, could be described as  $\text{Cu}^+ \cdots \text{Cu}^{2+} \cdots \text{O}^-$  [50]. In the present study, XRD and TPR results have shown that there are well-dispersed copper species (including isolated copper species), and large copper oxide particles. The former has a strong interaction with the surface of Si-TiNbO<sub>5</sub> support. XPS results showed that  $\text{Cu}^+$  existed in the catalysts before and after NO decomposition. By adopting a similar pathway to that on Cu-ZSM-5, it is not difficult to explain the catalytic behaviors of Cu/Si-TiNbO<sub>5</sub> for NO decomposition. As the Cu loading increased up to 3.5 wt.%, the surface of the support was completely covered and had the most reactive sites, so the catalyst showed the highest activity. As the Cu loading further increased, part of the active copper species aggregated to form large copper oxide particles and lost their catalytic activity. As shown in Table 2, at lower temperature ( $\leq 550^\circ\text{C}$ ), 2.0 wt.% Cu/Si-TiNbO<sub>5</sub> catalyst had the highest apparent turnover frequency. For 1.0 wt.% Cu/Si-TiNbO<sub>5</sub>, its Cu content was too low to form high active dimer ( $\text{Cu}_2\text{O}^{2+}$ ), so the specific activity was low. Similar phenomenon was also found on Cu-ZSM-5 and on Cu-mesoporous-silica-alumina catalysts [21,51]. For 2.0 wt.% Cu/Si-TiNbO<sub>5</sub>, more binuclear copper sites were formed and, therefore, led to high specific activity. As the Cu content further increased, large copper oxide particles appeared so that the specific activities rapidly diminished. At higher temperature ( $> 550^\circ\text{C}$ ), for 1.0 wt.% Cu/Si-TiNbO<sub>5</sub> catalysts, the turnover frequency drastically increased with the temperature and the catalyst showed the highest specific activity. On the one hand, isolated Cu species formed more active dimeric ones at the elevated temperature. On the other

hand, isolated Cu species may also become more active than other Cu species.

## 5. Conclusion

Silica-pillared layered titanoniobate supported Cu catalysts were first found highly active for the decomposition of NO in the wide range of space velocity. H<sub>2</sub>-TPR of Cu/Si-TiNbO<sub>5</sub> showed the existence of different copper oxide species. Copper species well dispersed on the support were reduced more easily than unsupported CuO. XPS and AES showed that there existed  $\text{Cu}^+$  in Cu/Si-TiNbO<sub>5</sub> both before and after the reaction. Well-dispersed copper species close to the support were active for the decomposition of NO. The pathway for decomposition of NO over Cu/Si-TiNbO<sub>5</sub> might be similar with that on Cu-ZSM-5. Dimeric copper species might be the most active sites in the reaction. This study may open up a new field for the application of metal oxides pillared layered materials in catalysis and be of importance in developing a new family of the catalysts highly active for the removal of NO.

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