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# Enhancing the low temperature NH<sub>3</sub>-SCR activity of FeTiO<sub>x</sub> catalysts via Cu doping: a combination of experimental and theoretical study†

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A series of Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts with variable Cu doping amounts was directly synthesized by the sol-gel method and their catalytic performances were tested for the selective catalytic reduction of NO with ammonia. The highest activity was achieved on Fe<sub>0.9</sub>Cu<sub>0.1</sub>Ti catalyst. NO conversion was above 80% and N<sub>2</sub> selectivity exceeded 90% on this catalyst in the temperature range of 200–375 °C. High NO and NH<sub>3</sub> oxidation activities facilitated the high NH<sub>3</sub>-SCR activities of the catalysts in the low temperature range, while too strong NH<sub>3</sub> oxidation ability resulted in the decline of NH<sub>3</sub>-SCR activity. DFT calculations based on the Fe and Cu co-doping TiO<sub>2</sub> model showed that the barrier of NH<sub>3</sub> activation is dramatically reduced as compared to pure Fe doping. This is due to the lowered p-band of lattice O. However, such activated O will also strongly decrease the barrier for the dissociation of NH<sub>2</sub> to NH species, which will lead to the formation of N<sub>2</sub>O. Both Brønsted and Lewis acid sites over Fe<sub>0.9</sub>Cu<sub>0.1</sub>Ti catalyst are involved in the NH<sub>3</sub>-SCR reaction. The adsorption of NO<sub>x</sub> is strong in the low temperature range, and large amounts of nitrates were decomposed on the catalyst surface in the high temperature range.

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## 1. Introduction

Fast urbanization and the rapid development of industry have caused serious air pollution and stringent regulations are being released with growing environmental awareness. It is generally considered that air pollution is predominantly from the combustion processes of fossil fuels in power plants, vehicles and other incineration processes. Among various air contaminants, nitrogen oxides (NO<sub>x</sub>) are notable and are known as the major causes of photochemical smog, haze, acid rain, ozone depletion and the greenhouse effect. Selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> (NH<sub>3</sub>-SCR) is a powerful technique for the abatement of NO<sub>x</sub> from stationary sources. WO<sub>3</sub> (MoO<sub>3</sub>) modified V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> are the current commercially used catalysts for NH<sub>3</sub>-SCR in industry. However, some disadvantages still exist in these catalyst systems, including high working temperature, toxicity of vanadium species and low N<sub>2</sub> selectivity at high temperatures. Therefore, many researchers are trying to develop new NH<sub>3</sub>-SCR catalysts with high deNO<sub>x</sub> efficiency, high N<sub>2</sub>

selectivity, excellent hydrothermal stability and insensitivity to co-existing poisoning components in the SCR atmosphere, such as H<sub>2</sub>O, SO<sub>2</sub> or alkali metals.<sup>1–3</sup>

Recently, Fe-based catalysts have attracted much attention for the SCR reaction.<sup>4–6</sup> For example, FeTiO<sub>x</sub> catalyst is more active than crystalline Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. The active iron titanate crystallites in FeTiO<sub>x</sub> catalyst prepared at low calcination temperature were mainly in the form of a specific edge-shared Fe<sup>3+</sup>–(O)<sub>2</sub>–Ti<sup>4+</sup> structure. However, the catalytic activity of FeTiO<sub>x</sub> catalyst is low at low temperature.<sup>7–10</sup> It is essential to enhance the low-temperature SCR activity of FeTiO<sub>x</sub> catalyst. Among the alternatives of active components examined for the low-temperature SCR reaction, copper has been widely explored owing to its efficacy and relatively low cost.<sup>11–14</sup> It is well known that the SCR performance of catalysts depends on the dispersion, nuclearity and oxidation state of the active components, which could be efficiently controlled by the preparation method.<sup>15,16</sup>

In the present work, a series of Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts with variable Cu doping amounts was directly synthesized by the sol-gel method and applied in the NH<sub>3</sub>-SCR process. The obtained Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> catalysts exhibited excellent SCR activity. Based on this result, the effects of Cu substitution amounts on the structure, acidity and redox properties of the Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts were also studied. The reactivity of surface-adsorbed NH<sub>3</sub> and NO<sub>x</sub> species on the Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> catalysts was investigated using *in situ* diffused reflectance infrared Fourier transformed spectroscopy (DRIFTS) technique.

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## 2. Experimental and computational details

### 2.1. Catalyst preparation

$\text{Fe}_\alpha\text{Cu}_{1-\alpha}\text{TiO}_x$  catalysts were prepared by the sol-gel method. All chemicals used were of analytical grade. A solution of 34 ml of butyl titanate (Sinopharm Chemical Reagent Co., Ltd,  $\geq 98.0\%$ ) and 136 ml of anhydrous ethanol (Sinopharm Chemical Reagent Co., Ltd,  $\geq 99.7\%$ ) was added dropwise to another solution of 34 ml of deionized water, 34 ml of anhydrous ethanol, 6.8 ml of nitric acid (Sinopharm Chemical Reagent Co., Ltd, 65.0–68.0%) and a certain amount of ferric nitrate (Sinopharm Chemical Reagent Co., Ltd,  $\geq 98.0\%$ ) and copper nitrate (Sinopharm Chemical Reagent Co., Ltd,  $\geq 98.0\%$ ) at room temperature under vigorous stirring to carry out hydrolysis. After continuously stirring for 3 h, the yellowish transparent sol was yielded. Subsequently, the sol was dried at 80 °C for 24 h to form a xerogel. After being crushed and sieved through a 60–100 mesh, the xerogel was calcinated at 500 °C for 5 h in air. The catalysts were denoted as  $\text{Fe}_\alpha\text{Cu}_{1-\alpha}\text{TiO}_x$ , where  $\alpha$  represents the molar ratio of  $n(\text{Fe})/n(\text{Fe} + \text{Cu})$ .

### 2.2. Physical and chemical characterization

The crystal structures of the fresh catalysts were determined with a powder X-ray diffractometer using  $\text{Cu K}\alpha$  ( $\lambda = 0.1542 \text{ nm}$ ) radiation combined with a nickel filter operating at 40 kV and 10 Ma (Shimadzu, Japan). The diffractometer data were recorded for  $2\theta$  values from 10° to 80° at a scanning rate of 4°  $\text{min}^{-1}$ . The patterns were compared with ICDD files for phase identification.

The Brunauer–Emmett–Teller (BET) surface areas were measured by  $\text{N}_2$  adsorption and desorption (Quantachrome Instruments, USA). The samples were degassed at 200 °C for 12 h.

TEM images were obtained using a JEOL JEM 2100 electron microscope equipped with a field emission source at an accelerating voltage of 200 kV. Drops of the suspension were applied and, after drying, the fine particles were well dispersed on a copper grid coated with carbon. The elemental local mapping was acquired by energy-dispersive spectroscopy (EDS) using a Tecnai F20 electron microscope equipped with a STEM unit and a CCD detector.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a standard AlK source (1486.6 eV) working at 350 W (XSAM800, Kratos Analytical Ltd, UK). The working pressure was less than  $2 \times 10^{-7}$  Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f<sub>7/2</sub> line to lie at 84.0 eV with respect to the Fermi energy level. The binding energies of Ce 3d and O 1s were calibrated using the C 1s peak (BE = 284.8 eV) as the standard.

Temperature-programmed reduction with  $\text{H}_2$  ( $\text{H}_2$ -TPR) experiments were performed using a Quantachrome Instruments Autosorb IQ. A 100 mg sample was pretreated under Ar by calcination at 300 °C for 1 h and subsequently cooled to 30 °C. Afterwards, 10%  $\text{H}_2/\text{Ar}$  flow (60  $\text{ml min}^{-1}$ ) was passed over the

catalyst bed while the temperature was ramped from 30 to 800 °C at a heating rate of 10 °C  $\text{min}^{-1}$ .

The nature of the acid sites of the catalysts was determined by pyridine-IR (Py-IR) on a Magna IR 560 FT-IR instrument with a resolution of 4  $\text{cm}^{-1}$ . The samples were dehydrated at 500 °C for 5 h under a vacuum of  $1.33 \times 10^{-3}$  Pa, followed by the adsorption of purified pyridine vapor at room temperature for 20 min. The system was then degassed and evacuated at different temperatures, and Py-IR spectra were recorded.

*In situ* DRIFTS spectra were recorded using a thermo Nicolet IS50 spectrometer, which was equipped with a high-temperature environmental cell fitted with a ZnSe window and an MCT detector cooled with liquid  $\text{N}_2$ . The catalyst was loaded in the Harrick IR cell and heated to 400 °C under  $\text{N}_2$  at a total flow rate of 50  $\text{ml min}^{-1}$  for 60 min to remove adsorbed impurities. A background spectrum was collected under a flowing  $\text{N}_2$  atmosphere and was subtracted from the sample spectra. The DRIFTS spectra were recorded by accumulating 32 scans with a resolution of 4  $\text{cm}^{-1}$ .

### 2.3. Activity measurements

The activity tests of the various catalysts for the  $\text{NH}_3$ -SCR of NO were carried out in a fixed bed quartz reactor (i.d. 6 mm). The feed gas mixture consisted of 1000 ppm of NO, 1000 ppm of  $\text{NH}_3$ , 3 vol% of  $\text{O}_2$  and Ar-balanced gas. A total flow rate of 500  $\text{ml min}^{-1}$  was maintained for all experiments. The concentrations of NO in the inlet and outlet gas were measured by a flue gas analyzer (Model-4000VM, SIGNAL International Ltd., UK). Meanwhile, the concentrations of  $\text{NH}_3$ , NO,  $\text{NO}_2$  and  $\text{N}_2\text{O}$  were measured by an FTIR spectrometer (Nicolet IS50). All catalysts were kept on stream at each temperature for 30 min. NO conversion was defined as follows:

$$\text{NO conversion}(\%) = \frac{\text{NO}_{(\text{inlet})} - \text{NO}_{(\text{outlet})}}{\text{NO}_{(\text{inlet})}} \times 100\% \quad (1)$$

where  $\text{NO}_{(\text{inlet})}$  represents the NO concentration in the inlet (ppm) and  $\text{NO}_{(\text{outlet})}$  represents the NO concentration in the outlet (ppm).

$\text{N}_2$  selectivity in the SCR reaction was calculated from eqn (2).

$$\text{N}_2 \text{ selectivity}(\%) = \frac{2[\text{N}_2]_{\text{out}}}{2[\text{N}_2]_{\text{out}} + 2[\text{N}_2\text{O}]_{\text{out}} + [\text{NO}_2]_{\text{out}}} \times 100\% \quad (2)$$

### 2.4. Computational details

In this work, the Vienna ab initio simulation package (VASP)<sup>17,18</sup> was used to calculate all states with the electron-exchange correlation effect described by the Perdew–Burke–Ernzerhof functional within the generalized gradient approximation (GGA-PBE).<sup>19</sup> The calculations involved on-site Coulomb corrections<sup>20</sup> (DFT+U,  $U_{\text{eff}} = 4.2 \text{ eV}$  for Ti 3d states, 6.0 eV for Cu 3d state, 4.5 eV for Mn 3d states). The spin-polarized calculations were performed. PAW pseudopotential was used to describe the core-valence electron interaction.<sup>21</sup> A plane-wave basis set with an energy cutoff of 400 eV was used in this



work. The climbing nudged elastic band method (CI-NEB)<sup>22,23</sup> was employed to locate the transition states. The anatase TiO<sub>2</sub> (101) surface was presented by a six-layer slab model with a vacuum gap of 15 Å. For all the surface calculations, the model was a periodic slab with a (2 × 2) surface unit cell. A Monkhorst pack 2 × 2 × 1 *k*-point mesh was used for the Brillouin zone integration. During structural optimizations, all of the atoms except those in the bottom two TiO<sub>2</sub> layers of the slab were allowed to relax until atom forces were smaller than 0.05 eV Å<sup>-1</sup>. Adsorption energy was calculated using the following expression:  $E_{\text{ad}} = E_{\text{tot}} - E_{\text{slab}} - E_{\text{x}}$ .  $E_{\text{tot}}$  is the total energy of the combined system with the adsorbate X bound to the slab,  $E_{\text{slab}}$  is the energy of the slab alone, and  $E_{\text{x}}$  is the energy of the adsorbate in the gas phase. According to this definition, exothermic adsorption results in a negative value of  $E_{\text{ad}}$ .

### 3. Results and discussion

#### 3.1. SCR performance

Fig. 1 shows the NH<sub>3</sub>-SCR performance as a function of temperature on the Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts with GHSV = 50 000 h<sup>-1</sup>. The FeTiO<sub>x</sub> catalyst showed very narrow operation temperature windows, and 80% NO conversion was obtained at a higher temperature of 275 °C. The temperature at which NO conversion exceeded 80% decreased to 255 °C for Fe<sub>0.95</sub>Cu<sub>0.05</sub>TiO<sub>x</sub> and about 150 °C for CuTiO<sub>x</sub>. The temperature range for optimum NO reduction (>80%) extends toward lower temperatures. Thus, copper oxide plays an important role in the low-temperature NH<sub>3</sub>-SCR reaction.<sup>16</sup> Among these catalysts, the Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> catalyst with the molar ratio of Fe : Cu = 9 : 1 showed the best activity with NO conversion above 80% from 200 °C to 375 °C. Comparatively, the maximal NO conversion on CuTiO<sub>x</sub> only reached 89%, indicating that CuO<sub>x</sub> addition can remarkably enhance the low-temperature NH<sub>3</sub>-SCR activity of FeTiO<sub>x</sub> catalysts and broaden the temperature window for NO conversion.

Fig. 1b shows the NH<sub>3</sub> conversion as a function of temperature over various catalysts during the NH<sub>3</sub>-SCR reaction. The NH<sub>3</sub> conversion monotonously increased with increasing of the Cu doping amount in the Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts. At a temperature of 150 °C the CuTiO<sub>x</sub> catalysts gave an ammonia conversion above 80% and this was maintained above 90% in the temperature range of 200–400 °C. The results indicate that gaseous NH<sub>3</sub> is activated more easily on Cu-containing catalysts, thus the Cu-containing catalysts showed better low-temperature activity than FeTiO<sub>x</sub> catalysts.

DFT calculations were then performed to gain a better understanding of the role of doping Cu in enhancing the reactivity. As shown in Fig. S1,† NH<sub>3</sub> adsorbs on the Cu-Fe-TiO<sub>2</sub> surface with an adsorption energy of -0.92 eV, 0.08 eV stronger than that on the Fe-TiO<sub>2</sub> surface. This suggests that Cu doping can slightly enhance NH<sub>3</sub> adsorption. As shown in previous studies, the dissociation of adsorbing NH<sub>3</sub> is the rate-limiting step of the NH<sub>3</sub>-SCR reaction.<sup>24–26</sup> The activation barrier of this step was calculated on the two comparative models (Fe-Cu-TiO<sub>2</sub> and Fe-TiO<sub>2</sub>). The H of adsorbed NH<sub>3</sub> can be dissociated to surface O atom to form NH<sub>2</sub> species with an energy barrier of

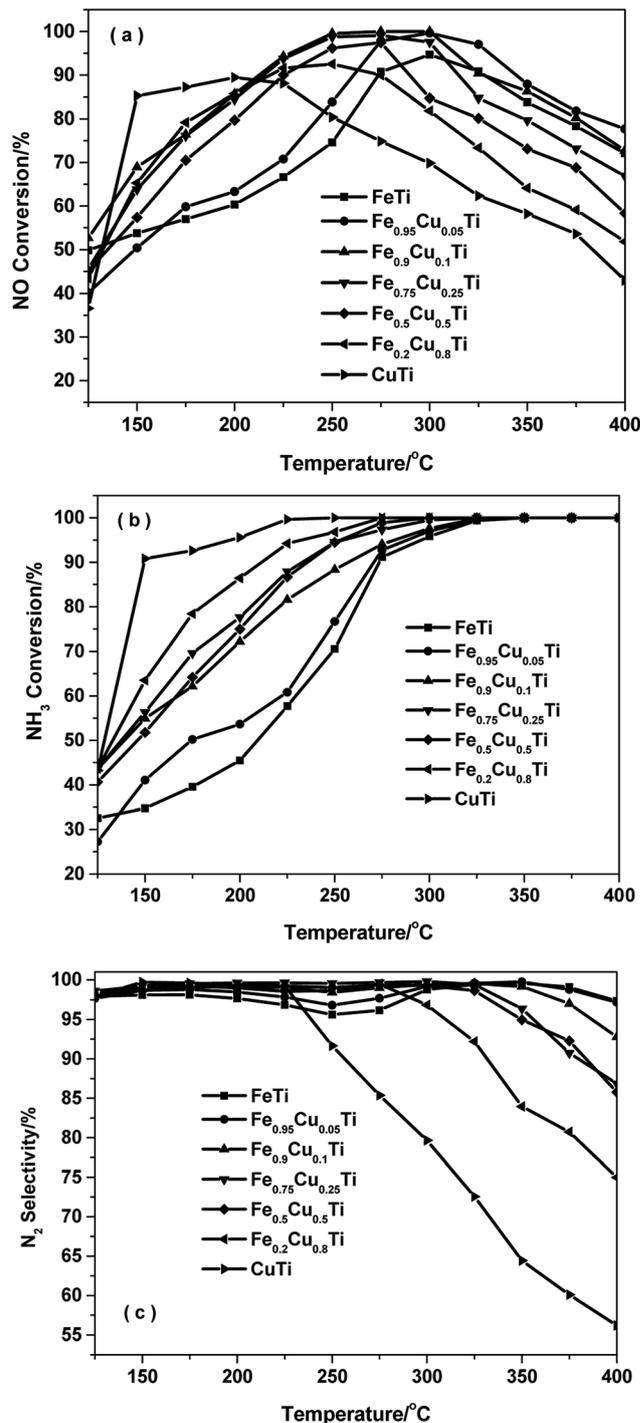


Fig. 1 NH<sub>3</sub>-SCR performance as a function of temperature on Fe<sub>α</sub>-Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts with GHSV = 50 000 h<sup>-1</sup>. (a) NO conversion, (b) NH<sub>3</sub> conversion and (c) N<sub>2</sub> selectivity.

0.64 eV, which is 0.71 eV lower than that on Fe-TiO<sub>2</sub>. The lower energy barrier of NH<sub>3</sub> dissociation indicates higher SCR activity, consistent with the experimental results. The calculated density of states (DOS) (Fig. 2a) shows that the energy level of the conduction band of the active O p on Cu-Fe-TiO<sub>2</sub> is lower than that on Fe-TiO<sub>2</sub>. This is owing to the strong interaction between



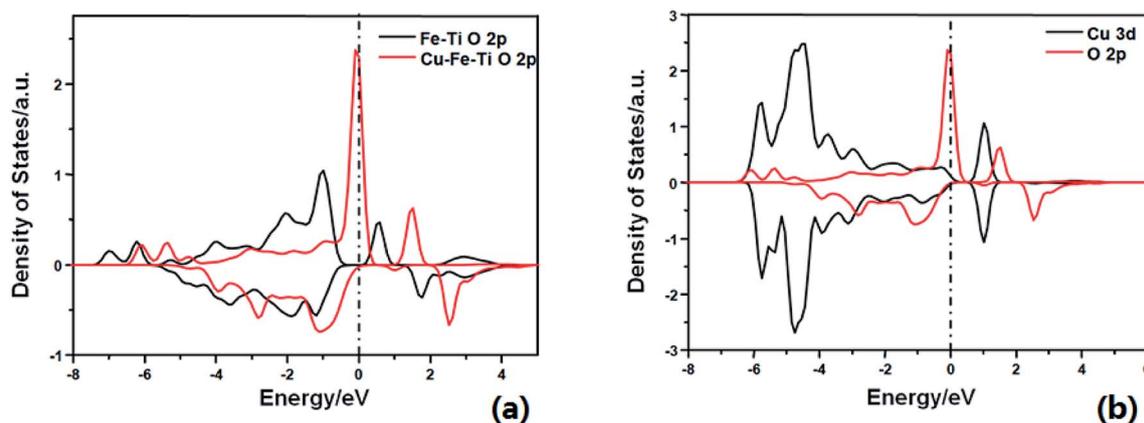


Fig. 2 Calculated projected density of states for (a) O 2p on Fe-TiO<sub>2</sub> surface (black) and Cu-Fe-TiO<sub>2</sub> surface (red); (b) Cu 3d (black) and O 2p (red) on Cu-Fe-TiO<sub>2</sub> surface.

Cu d bands and the O p band, which strongly changed the electron state of the neighboring O atom (Fig. 2b). From the electronic point of view, the essence of NH<sub>3</sub> dissociation with one H to the lattice O involves one electron being added to the conduction band of the O p orbital. The lower the conduction band, the easier the process. This explains the calculated lower energy barrier.

Fig. 1c shows the N<sub>2</sub> selectivity for the NH<sub>3</sub>-SCR of NO over Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts. Although the substitution of Fe by Cu in iron titanate catalyst could enhance the low-temperature SCR activity, the N<sub>2</sub> selectivity had an obvious decrease owing to the production of N<sub>2</sub>O with the increasing of the Cu molar amount, especially at high temperatures above 250 °C. The further dissociation of NH<sub>2</sub> to NH will lead to the formation of N<sub>2</sub>O. The calculated energy barrier is 0.76 eV for this step on Fe-Cu-TiO<sub>2</sub>, which is 0.38 eV lower than NH<sub>2</sub> dissociation on Fe-TiO<sub>2</sub>. This explains the experimental result that the N<sub>2</sub> selectivity had an obvious decrease owing to the production of N<sub>2</sub>O on the Cu-Fe-TiO<sub>2</sub> catalyst.

### 3.2. NH<sub>3</sub> and NO oxidation activities of Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts

A previous study<sup>13</sup> showed that the N<sub>2</sub> selectivity in the SCR reaction had a strong inverse correlation with the oxidation of NH<sub>3</sub>, therefore separate NH<sub>3</sub> oxidation experiments were also conducted over Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts. As shown in Fig. 3, the NH<sub>3</sub> conversions had an obvious enhancement with the increasing of Cu substitution amounts, and the highest NH<sub>3</sub> conversions were obtained over the CuTiO<sub>x</sub> catalyst. However, the N<sub>2</sub> selectivity showed an obvious decrease in NH<sub>3</sub> oxidation reactions at the same time, which is in accordance with the changing trend of N<sub>2</sub> selectivity in the SCR reaction. This implies that although the NO oxidation activity is enhanced when Fe is partially substituted by Cu, which is beneficial to the promotion of SCR activity, the unselective oxidation of NH<sub>3</sub> to N<sub>2</sub>O, NO or NO<sub>2</sub> in the SCR conditions is also enhanced, resulting in the production of a large amount of by-products. There should be a compromise between the SCR activity and

N<sub>2</sub> selectivity when we determine on the Cu substitution amount in practical applications.

It was reported that the enhancement of NO oxidation to NO<sub>2</sub> over SCR catalysts could significantly promote the low-temperature activity owing to the occurrence of “fast SCR”: 4NH<sub>3</sub> + 2NO + 2NO<sub>2</sub> + O<sub>2</sub> → 4N<sub>2</sub> + 6H<sub>2</sub>O.<sup>27-29</sup> The effect of NO<sub>2</sub> and the detailed “fast SCR” reaction mechanism have been studied extensively over conventional V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and Fe-zeolite catalysts (such as Fe/HBEA and Fe/ZSM-5) by many researchers. In this study, the effect of Cu substitution amounts on the NO oxidation activity of iron titanate catalysts was also investigated and the results are shown in Fig. 4. With the increasing of Cu substitution amounts, the NO conversion to NO<sub>2</sub> showed an obvious enhancement, and the maximum conversions were obtained over CuTiO<sub>x</sub> catalyst. Although the NO oxidation activity of CuTiO<sub>x</sub> was higher than that of Fe<sub>0.9</sub>-Cu<sub>0.1</sub>TiO<sub>x</sub>, the SCR activity over the former catalyst was still much lower than that over the latter one, as shown in Fig. 4.

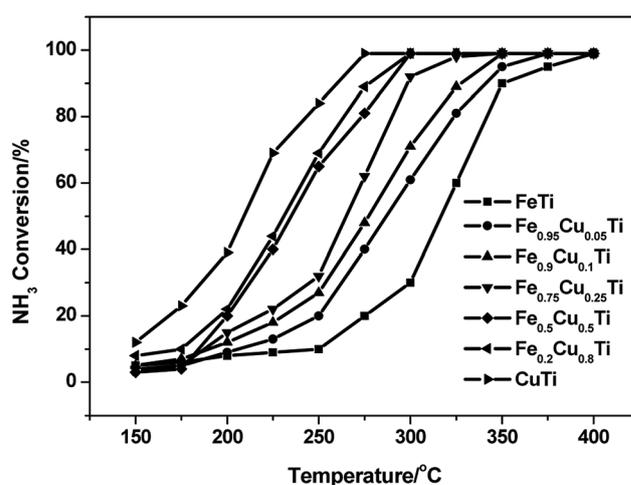


Fig. 3 NH<sub>3</sub> oxidation profile of Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts. Reaction conditions: [NH<sub>3</sub>] = 1000 ppm, [O<sub>2</sub>] = 3%, balance N<sub>2</sub> and GHSV = 50 000 h<sup>-1</sup>.



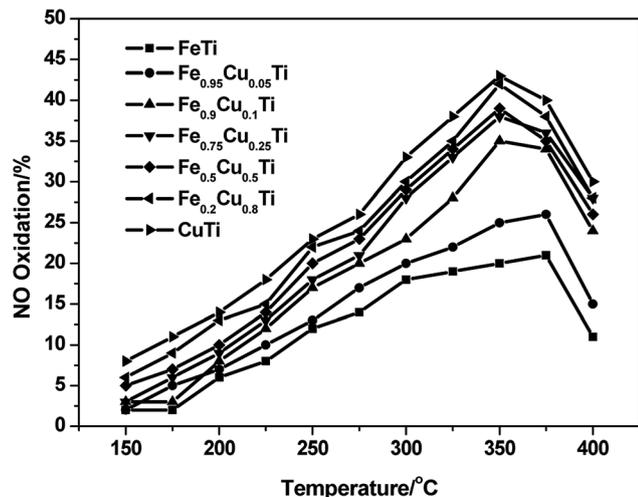


Fig. 4 NO oxidation profile of  $\text{Fe}_\alpha\text{Cu}_{1-\alpha}\text{TiO}_x$  catalysts. Reaction conditions:  $[\text{NO}] = 1000 \text{ ppm}$ ,  $[\text{O}_2] = 3\%$ , balance  $\text{N}_2$  and GHSV =  $50\,000 \text{ h}^{-1}$ .

This implies that the SCR activity over  $\text{CuTiO}_x$  catalyst is not just related to the NO oxidation activity.

### 3.3. XRD results

Powder XRD patterns of  $\text{Fe}_\alpha\text{Cu}_{1-\alpha}\text{TiO}_x$  catalysts are shown in Fig. 5.  $\text{FeTiO}_x$  catalyst showed no obvious sharp diffraction peaks besides some broad bumps, implying that this catalyst was mainly in the form of amorphous iron titanate, which were thought to be the real active phases. With the increasing of Cu molar amount from 0 to 0.25, XRD patterns of  $\text{Fe}_\alpha\text{Cu}_{1-\alpha}\text{TiO}_x$  catalysts exhibited no significant variation, indicating that these samples were still in an amorphous state. The part substitution of Fe by Cu did not destroy the catalyst structures. However, when Cu substitution amounts increased to above 0.25,  $\text{TiO}_2$  and  $\text{CuO}$  phase peak appeared, which indicated that

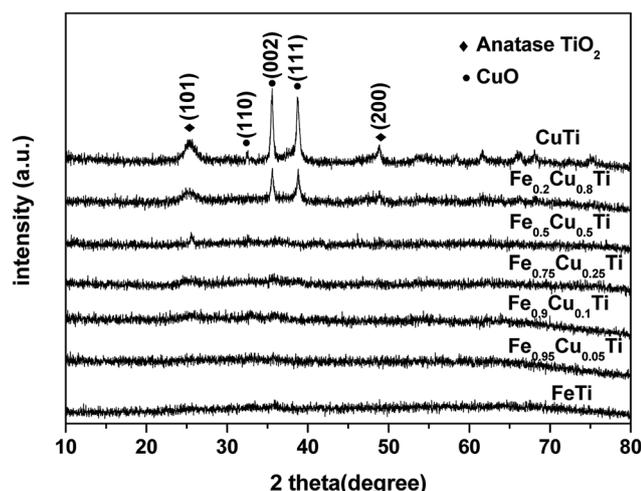


Fig. 5 X-ray diffraction patterns of  $\text{Fe}_\alpha\text{Cu}_{1-\alpha}\text{TiO}_x$ .

the amorphous state structure was destroyed. The negligible effect of increasing Cu amount above 0.25 on the SCR activity is related to this change.

### 3.4. BET results

Fig. S2† shows the nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves of the  $\text{Fe}_\alpha\text{Cu}_{1-\alpha}\text{TiO}_x$  catalysts. The isotherms for the  $\text{Fe}_\alpha\text{Cu}_{1-\alpha}\text{TiO}_x$  catalysts are similar to typical type IV isotherms, which are characteristic of mesoporous materials. In the diameter range below 3 nm, the adsorbed volume on the  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  catalyst was highest among all catalysts. This means that the  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  sample included the most abundant micropores or mesopores, which can supply a greater inner surface area for the occurrence of the SCR reaction. The BET surface areas in Table 1 also followed such a sequence, which is in good agreement with the sequence of SCR activity. The  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  catalyst exhibited the largest BET surface area, which is beneficial to the  $\text{NH}_3$ -SCR process.

### 3.5. TEM results

Fig. 6 shows the TEM/HRTEM images of the  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  and  $\text{Fe}_{0.5}\text{Cu}_{0.5}\text{TiO}_x$  catalysts. Both catalysts were made of nanoparticles in the size range of 15–30 nm, as shown in Fig. 6a and c. For the  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  catalyst, no interplanar distances of  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{TiO}_2$  were seen on the surface of the catalyst. This suggests the formation of the homogeneous phase of  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{TiO}_2$ , which is consistent with the XRD results. For the  $\text{Fe}_{0.5}\text{Cu}_{0.5}\text{TiO}_x$  catalyst, two phases with the interplanar spacing are shown in Fig. 6d, corresponding to the interplanar distances of  $\text{CuO}$  and  $\text{TiO}_2$  planes, respectively. The results mean that the amorphous state structure was destroyed on the  $\text{Fe}_{0.5}\text{Cu}_{0.5}\text{TiO}_x$  catalyst.

### 3.6. Py-IR results

FTIR spectroscopy of adsorbed pyridine was performed to study the acid properties of the  $\text{FeTiO}_x$  and  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  samples. As shown in Fig. 7, the bands located at  $1540$  and  $1640 \text{ cm}^{-1}$  are assigned to pyridinium ions adsorbed on Brønsted sites. The bands located at  $1440$ ,  $1455$  and  $1630 \text{ cm}^{-1}$  are due to pyridinium ions adsorbed on Lewis sites. Brønsted and Lewis acid sites were observed in both  $\text{FeTiO}_x$  and  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  catalysts, where Lewis acid sites prevail over Brønsted acid sites at  $200 \text{ }^\circ\text{C}$ .

Table 1 The textural and structural properties of all catalysts

Samples	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$V_{\text{mic}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	Average pore diameter (nm)
$\text{FeTiO}_x$	185.2	0.30	4.6
$\text{Fe}_{0.95}\text{Cu}_{0.05}\text{TiO}_x$	187.0	0.27	4.3
$\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$	244.5	0.27	5.1
$\text{Fe}_{0.75}\text{Cu}_{0.25}\text{TiO}_x$	121.2	0.23	5.1
$\text{Fe}_{0.5}\text{Cu}_{0.5}\text{TiO}_x$	128.1	0.23	4.8
$\text{Fe}_{0.2}\text{Cu}_{0.8}\text{TiO}_x$	104.7	0.21	5.2
$\text{CuTiO}_x$	89.1	0.20	5.9



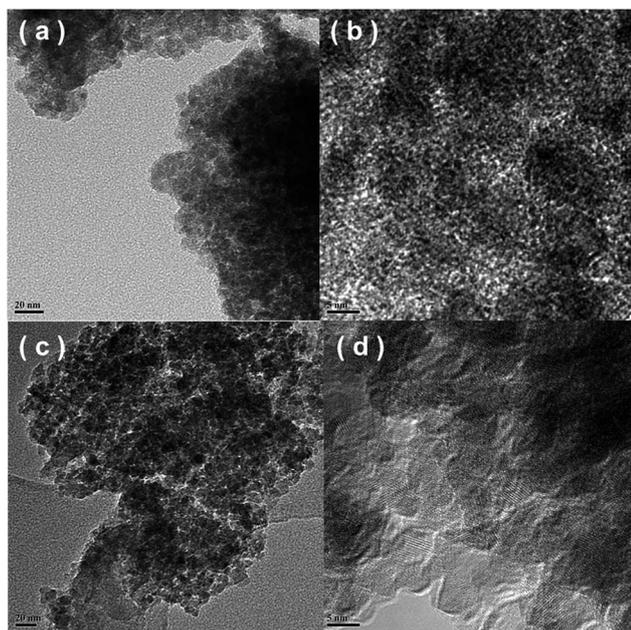


Fig. 6 TEM/HRTEM images of Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> (a and b) and Fe<sub>0.5</sub>Cu<sub>0.5</sub>TiO<sub>x</sub> (c and d).

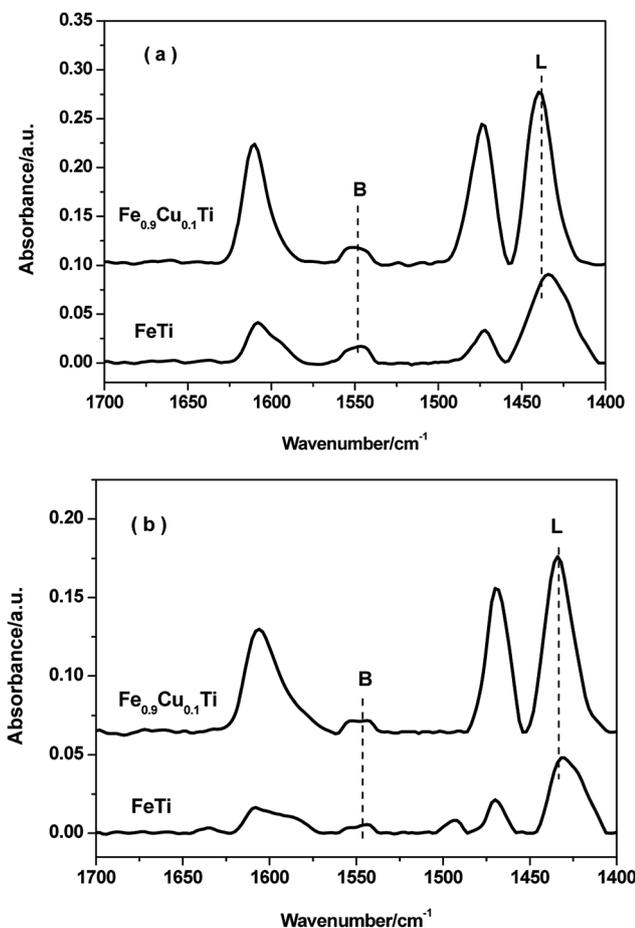


Fig. 7 FT-IR spectra of pyridine adsorbed on FeTiO<sub>x</sub> and Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> after degassing at 200 °C and 350 °C.

When the adsorption temperature was increased to 350 °C, the intensities of the Lewis and Brønsted peaks decreased. It can be seen that Lewis and Brønsted acid sites are more abundant in the Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> catalyst than in the FeTiO<sub>x</sub> catalyst. The more Lewis acid sites over the Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> catalyst would not be attributed to the addition of Cu substance with abundant Lewis acid sites, but the changes in catalyst structure and electron charge density caused by the generation of Ti–O–Fe mixed bonds. It has been reported that the acid sites may interact with the active components, and therefore inhibit the agglomeration of the active components. Moreover, the increasing of Lewis acid sites would promote the SCR performance by enhancing the activation of NH<sub>3</sub>.

### 3.7. XPS results

Fig. 8a shows the XPS results for Fe 2p. Two characteristic peaks ascribed to Fe 2p<sub>3/2</sub> at 710.1 eV and Fe 2p<sub>1/2</sub> at 723.7 eV appeared for each Fe-containing sample, indicating that the iron species in these samples are in the Fe<sup>3+</sup> oxidation state. With the increasing of Cu substitution amounts, the intensities of the Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> peaks gradually decreased owing to the concentration reduction of surface iron species. However, the corresponding binding energies do not show variation, implying that the differences in the SCR over these catalysts are not caused by the redox ability after changing the iron species state.

Fig. 8b shows the XPS spectra of Ti 2p in all catalysts. Two characteristic peaks at ca. 457.3 and 463.1 eV appear with the increasing of the Cu molar content from 0 to 0.5, which are assigned to Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub>. On further increasing the Cu doping amount, the binding energies of Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> in relevant samples are shifted toward higher BE by 0.5 eV. Combined with the XRD results, this phenomenon may be due to the phase transformation.

Fig. 8c shows XPS spectra of Cu 2p in all catalysts. The Cu 2p<sub>3/2</sub> signal is composed of two peaks at 933.6 eV and 934.5 eV, where the former is assigned to the presence of CuO species<sup>30,31</sup> and the latter to Cu<sup>2+</sup> species. Cu<sup>2+</sup> species are detected when the Cu doping amount is below 0.25. Further increasing the Cu doping amount to above 0.25, the catalysts are in the CuO phase. It indicates that the Cu<sup>2+</sup> species transform to the CuO phase when the Cu substitution amount increases to above 0.25. This result is also consistent with the XRD results. CuO could accelerate NH<sub>3</sub> oxidation and, as a result, the transformation of Cu species from Cu<sup>2+</sup> to CuO would cause the decrease of the selectivity of the Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts.

### 3.8. In situ DRIFTS studies

**3.8.1. Adsorption of NH<sub>3</sub>.** Fig. 9 shows the *in situ* DRIFT spectra of NH<sub>3</sub> adsorption over FeTiO<sub>x</sub> and Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> catalysts at different temperatures. When NH<sub>3</sub> was introduced into the DRIFTS cell at room temperature, several vibration bands could be detected in the range of 1000–4000 cm<sup>-1</sup>. For the FeTiO<sub>x</sub> catalyst (Fig. 9a), the bands at 1602 and 1209 cm<sup>-1</sup> can be assigned to the asymmetric and symmetric bending vibrations of the NH bond in the NH<sub>3</sub> coordinately linked to the



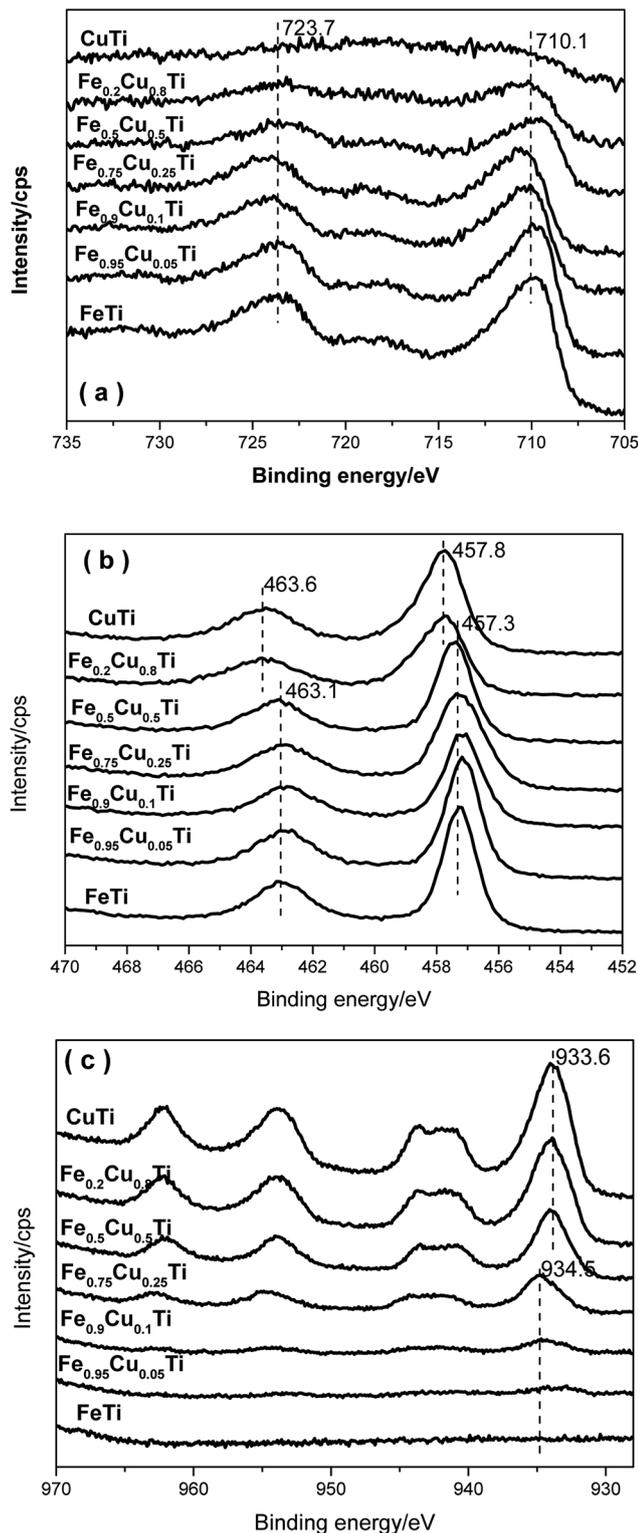


Fig. 8 XPS spectra of (a) Fe 2p, (b) Ti 2p and (c) Cu 2p in  $\text{Fe}_\alpha\text{Cu}_{1-\alpha}\text{TiO}_x$  catalysts.

Lewis acid site, respectively. The peaks at 3337, 3267 and 3174  $\text{cm}^{-1}$  can be ascribed to the N-H stretching vibration modes of the coordinated  $\text{NH}_3$ , while the band at 1456  $\text{cm}^{-1}$  is due to the asymmetric bending vibration of NH bond in  $\text{NH}_4^+$

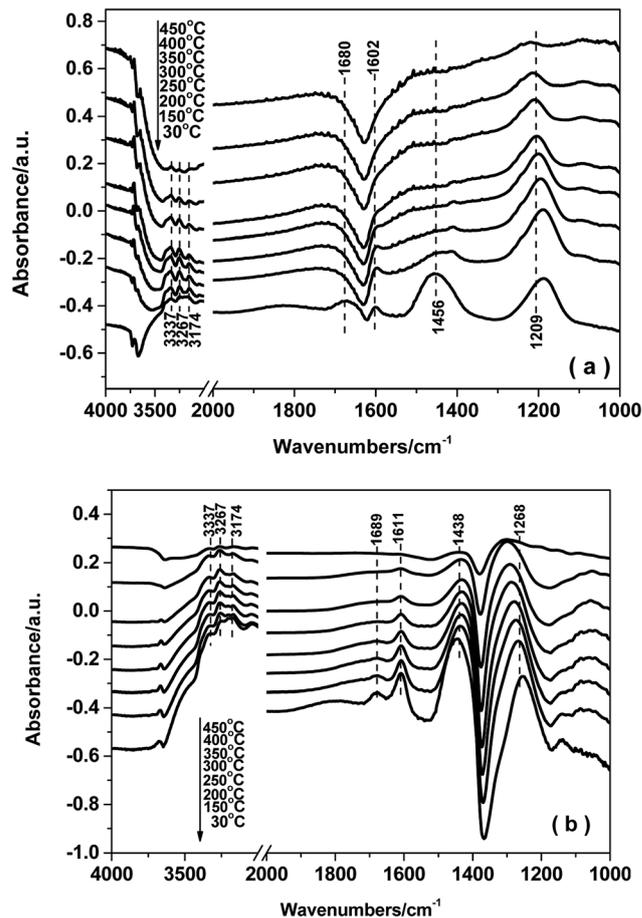


Fig. 9 *In situ* DRIFTS of  $\text{NH}_3$  desorption on  $\text{FeTiO}_x$  (a) and  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  (b).

chemisorbed on the Brønsted acid site.<sup>32,33</sup> These adsorbed  $\text{NH}_3$  species decreased with the increasing of the temperature and the band attributed to the Brønsted acid site disappears at 200 °C. Fig. 9b shows the *in situ* DRIFT spectra of  $\text{NH}_3$  adsorption over the  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  catalyst. Both the intensities of the Lewis acid site and Brønsted acid sites on  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  catalyst are higher than those on  $\text{FeTiO}_x$  catalyst. It is also noticeable that the band attributed to the Brønsted acid site does not disappear completely even at 450 °C. The obtained results suggested that there are more abundant acid sites and the Brønsted acid sites are more stable with the introduction of Cu. Previous reports showed that Brønsted acid sites were beneficial to the adsorption of  $\text{NH}_3$ , thus improving the low-temperature activity.

**3.8.2. Co-adsorption of NO and  $\text{O}_2$ .** Fig. 10a shows the *in situ* DRIFT spectra of NO +  $\text{O}_2$  desorption on the  $\text{FeTiO}_x$  catalyst at different temperatures. The peaks at 1605, 1579, 1294 and 1254  $\text{cm}^{-1}$  were attributed to the asymmetric frequencies of bridged nitrate (1605 and 1254  $\text{cm}^{-1}$ ), bidentate nitrate (1579  $\text{cm}^{-1}$ ), and monodentate nitrate (1294  $\text{cm}^{-1}$ ) at room temperature. With the introduction of Cu, a new peak at 1897  $\text{cm}^{-1}$  at room temperature appeared in Fig. 10b, which was assigned to the asymmetric frequency of  $\text{Cu}^{2+}\text{-NO}$ .<sup>34,35</sup>



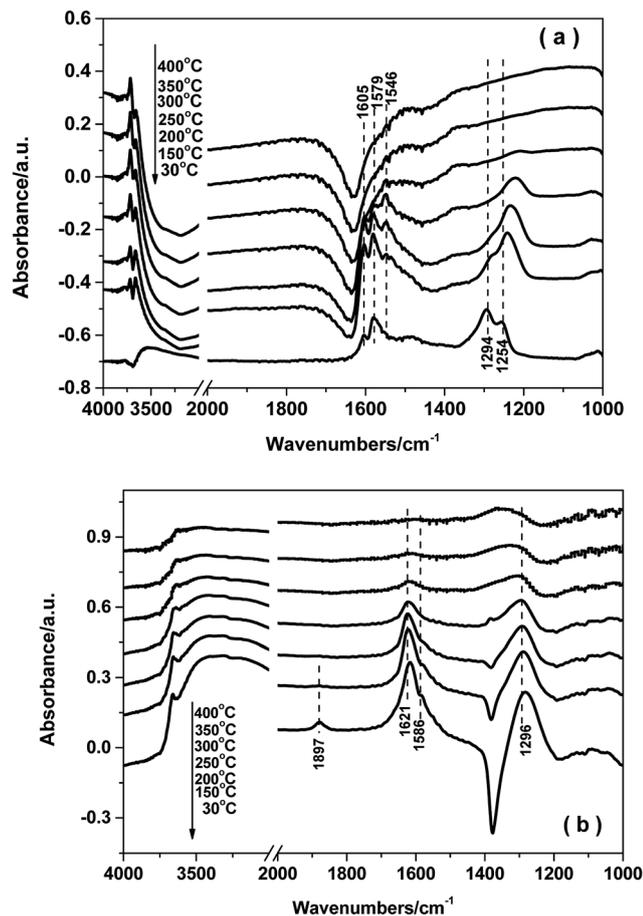


Fig. 10 *In situ* DRIFTS of NO + O<sub>2</sub> desorption on FeTiO<sub>x</sub> (a) and Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> (b).

With the increasing of the temperature to 250 °C, all bands attributed to NO<sub>x</sub> adspecies vanished instantly, indicating that the absorbed nitrate and nitrite species were decomposed. This result indicated that the adsorption of nitrate species was decomposed at high temperature, leading to more active sites being available for the adsorption and activation of NH<sub>3</sub>. Thus a higher catalytic activity was obtained. It is noted that the intensity of NO<sub>x</sub> adspecies was strong below 200 °C. The results indicated that NO<sub>x</sub> adspecies were easily adsorbed at low temperature on the catalysts, which was beneficial to the NH<sub>3</sub>-SCR process at low temperature *via* L-H mechanism.

**3.8.3. Reaction between nitrogen oxides and ammonia adspecies.** Fig. 11 shows the *in situ* DRIFT spectra of the FeTiO<sub>x</sub> and Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> catalysts as a function of time in a flow of NO + O<sub>2</sub> after the catalysts were pre-exposed to a flow of NH<sub>3</sub>. The coordinated NH<sub>3</sub> on Lewis and Brønsted acid sites was formed on the catalysts with feeding NH<sub>3</sub>. All bands due to ammonia adspecies diminished in 10 min after the catalysts were purged by NO + O<sub>2</sub>, and subsequently NO<sub>x</sub> adspecies were observed. NO<sub>x</sub> readily reacted with surface-active NH<sub>3</sub> species over the Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalyst. It could be concluded that the adsorbed NH<sub>3</sub> on the Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalyst would react with gas-phase NO (Eley-Rideal mechanism) to form N<sub>2</sub> at 250 °C.

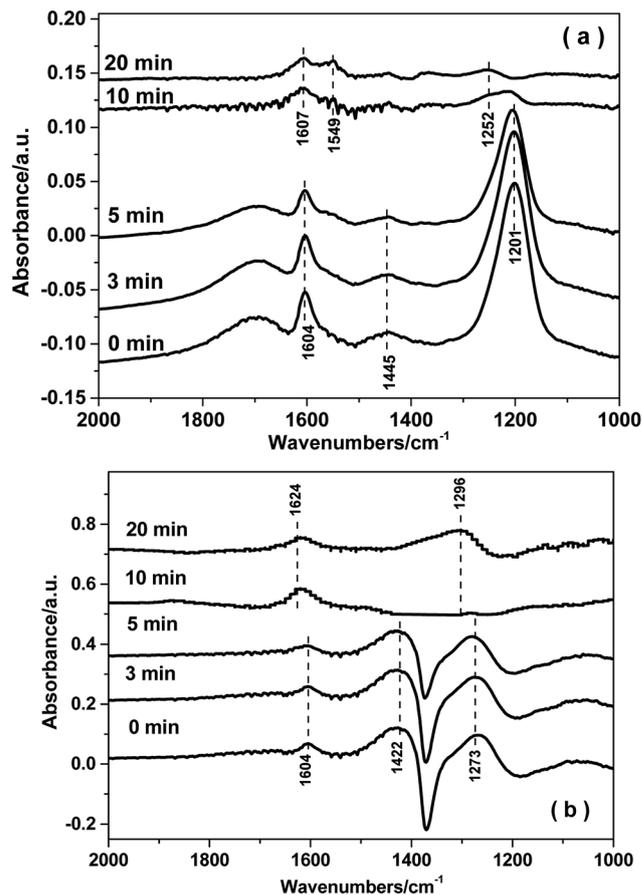


Fig. 11 *In situ* DRIFTS over FeTiO<sub>x</sub> (a) and Fe<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>x</sub> (b) as a function of time in a flow of NO + O<sub>2</sub> after the catalysts were pre-exposed to a flow of NH<sub>3</sub> for 60 min followed by N<sub>2</sub> purging for 30 min at 250 °C.

## 4. Conclusions

A series of Fe<sub>α</sub>Cu<sub>1-α</sub>TiO<sub>x</sub> catalysts with variable Cu doping amounts was directly synthesized by the sol-gel method, and their catalytic performances were tested for the selective catalytic reduction of NO with ammonia. The partial substitution of Fe by Cu could significantly promote the SCR activity of iron titanate catalysts, especially in the low temperature range. The highest activity was achieved on Fe<sub>0.9</sub>Cu<sub>0.1</sub>Ti catalyst. NO conversion was above 80% and N<sub>2</sub> selectivity exceeded 90% on this catalyst in the temperature range of 200–375 °C. However, the N<sub>2</sub> selectivity showed an obvious decrease with the increasing of Cu substitution amounts, and there should be a compromise between the SCR activity and N<sub>2</sub> selectivity when we determine the Cu substitution amount in practical industrial applications.

High NO and NH<sub>3</sub> oxidation activities facilitated the high NH<sub>3</sub>-SCR activities of the catalysts in the low-temperature range, while too strong NH<sub>3</sub> oxidation ability resulted in the decline of NH<sub>3</sub>-SCR activity. DFT calculations show that the barrier of NH<sub>3</sub> activation is dramatically reduced with the doping of both Cu and Fe owing to the lowered p-band of lattice O. However, such



activated O will also strongly decrease the barrier for the dissociation of  $\text{NH}_2$  to NH species, which will lead to the formation of  $\text{N}_2\text{O}$  and, accordingly, the decrease of  $\text{N}_2$  selectivity.

The reaction mechanism for  $\text{NH}_3$ -SCR over the  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{-TiO}_x$  catalyst was studied by means of *in situ* DRIFT spectroscopy. The results demonstrated that both Brønsted and Lewis acid sites over  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{Ti}$  catalyst were active in the  $\text{NH}_3$ -SCR reaction. On the one hand,  $\text{NO}_x$  adspecies were easily adsorbed at low temperature on the  $\text{Fe}_{0.9}\text{Cu}_{0.1}\text{TiO}_x$  catalyst, which were beneficial to the  $\text{NH}_3$ -SCR process at low temperature via the L-H mechanism. On the other hand, the adsorption of nitrate species was decomposed at high temperature, leading to more active sites available for the adsorption and activation of  $\text{NH}_3$ . Thus a higher catalytic activity was obtained.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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