


 Cite this: *RSC Adv.*, 2022, 12, 10142

DeNO_x performance enhancement of Cu-based oxides *via* employing a TiO₂ phase to modify LDH precursors†

 Yali Du,^{‡a} Xuezhen Liu,^{‡ab} Jiangning Liu,^b Rongting Du^b and Xu Wu^{ID*bc}

CuAl-LDO, CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalysts were obtained from TiO₂ modified LDHs precursor which were prepared by *in situ* assembly method. Then catalysts were evaluated in the selective catalytic reduction of NO_x with NH₃(NH₃-SCR), and the results showed that the CuAl-LDO/TiO₂NTs catalyst exhibited preferable deNO_x performance (more than 80% NO_x conversion and higher than 90% N₂ selectivity at a temperature range of 210–330 °C) as well as good SO₂ resistance. With the aid of series of characterizations such as XRD, N₂ adsorption/desorption, XPS, NH₃-TPD, H₂-TPR, and *in situ* DRIFTS, it could be concluded that, doping TiO₂NTs afforded the catalyst larger specific surface area, more abundant surface chemisorption oxygen species and more excellent redox performance. Meanwhile, *In situ* DRIFTS evidenced that CuAl-LDO/TiO₂NTs catalyst has a strong adsorption capacity for the reaction gas, which is more conducive to the progress of the SCR reaction.

Received 16th January 2022

Accepted 24th March 2022

DOI: 10.1039/d2ra00316c

rsc.li/rsc-advances

1 Introduction

Nitrogen oxides (NO_x), released from stationary sources (such as coal-fired power plants), are major atmospheric pollutants which seriously threaten the ecological environment and human health.^{1,2} Selective catalytic reduction with NH₃ (NH₃-SCR) is considered as one of the most efficient technologies for removing NO_x.^{3–5} Nowadays, the commercial V₂O₅-WO₃/TiO₂ catalysts are widely applied in the NH₃-SCR field and exhibit excellent catalytic activity in the temperature range of 300–400 °C.^{3,6,7} However, there are still some practical problems of the catalysts, such as the toxicity of vanadium, low N₂ selectivity due to the formation of N₂O and high conversion of SO₂ to SO₃ at high temperature.^{8,9} Generally, the poison of SO₂ and dust can be avoided by placing an SCR reactor behind the dust removal and desulfurization equipment, resulting in the debasement of exit gas temperature, which cannot meet the optimum activity temperature window of V₂O₅-WO₃/TiO₂ catalysts.^{10–12} Thus, it would be necessary to develop more efficient and eco-friendlier deNO_x catalysts with non-vanadium-based at low temperatures.

At the present stage, many researchers consider the copper oxides as a potential candidate for the low-temperature SCR catalysts, including pure copper oxides, copper-based composite oxides and supported copper-based catalysts.^{13–16} Among them, copper-based composite oxides catalysts with excellent catalytic performance have recently attracted much attention. In recent years, it is well known that layered double oxides (LDO) from layered-double hydroxides (LDHs) demonstrated fine reaction activity in NH₃-SCR, especially the typical CuAl-LDO catalyst.^{17,18} For instance, Yan *et al.* reported a high-performance Cu-based oxides catalyst prepared from CuAl-LDHs precursor.¹⁹ In our previous work, it is also found that the CuAl-LDO catalysts derived from LDHs demonstrated better reaction activity in NH₃-SCR.¹⁸ However, due to its insufficient acidity, the CuAl-LDO catalyst afforded poor reaction activity at medium and high temperature in NH₃-SCR, which limited its further application.

As well known, titanium dioxide (TiO₂) has been found to be a valuable and environmentally friendly material with stable chemical properties.²⁰ At the same time, for transition metal oxide catalyst, the introduction of TiO₂ could improve the acid sites and chemical adsorption oxygen over the catalyst surface, enhance the adsorption and activation of NH₃ as well as resistance of SO₂.^{21–24} Based on the characteristic advantages of LDHs and TiO₂, it is promising to prepare well-behaved Cu–Ti composite oxide catalysts derived by LDHs. However, due to the Jahn–Teller distortion of Cu²⁺ ions, it is difficult to prepare CuTi-based LDHs by one step preparation. Here, desirable SCR catalyst of CuAl-LDO/TiO₂ was tentatively fabricated by modifying CuAl-LDHs with TiO₂ phase.

^aCollege of Chemistry and Chemical Engineering, Jinzhong University, Jinzhong 030619, P. R. China

^bCollege of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, P. R. China. E-mail: wuxu@tyut.edu.cn; Fax: +86-351-6018528; Tel: +86-351-6018528

^cShanxi Huadun Industrial Co., Ltd, Taiyuan 030062, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d2ra00316c

‡ These authors contributed equally to this work.



Herein, the CuAl-LDHs with titanium-based materials were assembled and calcined at high temperature. Subsequently, the catalytic performance of the obtained composite oxide catalysts was evaluated in NH_3 -SCR reaction. At the same time, the structural characteristics and the SCR performance of the catalysts were explored through a series of characterizations, such as XRD, N_2 adsorption/desorption, TEM, XPS, H_2 -TPR, NH_3 -TPD. The intrinsic difference between CuAl-LDO and CuAl-LDO/ TiO_2 -NTs catalysts derived by LDHs over the deNO_x activity was studied by *In situ* DRIFTS. This research might provide significant reference value for LDHs precursor in SCR application.

2 Materials and methods

2.1. Materials

TiO_2 (P25), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%), NaOH (96%) and Na_2CO_3 (99%) were obtained from the Sino-pharm Chemical Reagent Company. All chemicals were of analytical grade and were employed without further purification.

2.2. Sample preparation

2.2.1. Synthesis of TiO_2 NTs. The titanium-based materials used in this study were TiO_2 (P25) and TiO_2 nanotubes (TiO_2 -NTs) where the TiO_2 NTs were synthesized by hydrothermal method *via* TiO_2 (P25) as the precursor. The specific procedure is as follows: the P25 was added to the NaOH solution (10 M) to form a homogeneous mixture. After that, the mixture was transferred into a Teflon autoclave and reacted at 150 °C for 30 h. The slurry was filtered and washed initially with deionized water until the pH reached about 7 and mixed with 0.1 M H^+ solution to reach a pH value about 1. Finally, the obtained precipitate was washed until the filtrate was neutral and dried at 70 °C for 30 h. Then, the obtained powder was calcined at 400 °C for 2 h (the heating rate being 2 °C min^{-1}) to obtain titanium dioxide nanotubes (marked as TiO_2 NTs).

2.2.2. Preparation of catalyst. The CuAl-LDHs/ TiO_2 NTs and CuAl-LDHs/ TiO_2 precursors were prepared by *in situ* assembly method. In detail, a certain amount of TiO_2 NTs or TiO_2 was dispersed in 100 mL deionized water to form dispersion liquid (solution A). The mixed nitrate solution (0.12 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.04 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and mixed base solution (0.3 M NaOH and 0.1 M Na_2CO_3) were slowly dripped into a round-bottomed flask within solution A. After that, the mixed solution was hydrothermally treated at 65 °C for 10 h. The obtained LDHs slurry was filtered and washed, dried overnight at 70 °C to obtain LDHs powder which was denoted as CuAl-LDHs/ TiO_2 NTs or CuAl-LDHs/ TiO_2 . The CuAl-LDHs were also fabricated *via* the identical method without any addition of titanium dioxide in solution A. Then CuAl-LDO, CuAl-LDO/ TiO_2 NTs and CuAl-LDO/ TiO_2 catalysts were prepared *via* calcining LDHs powders at 500 °C for 5 h under nitrogen (80 mL min^{-1}).

2.3. Catalyst characterization

The phase structure of the LDHs and catalyst samples was analyzed by the Rigaku DX-2700 X-ray diffractometer

instrument, with $\text{Cu}/\text{K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at the 2θ of 5° to 85°. The morphology of the precursors was scanned and analyzed by the scanning electron microscope (SEM, Hitachi's SU8010 JEOL). The morphology and surface atomic concentration of catalyst was scanned and analyzed by SEM and EDS-mapping (Carl Zeiss GeminiSEM300, Germany). The surface textural structures of catalysts were operated on the ASAP-2460 physical adsorption instrument (Micromeritics, USA) at -196 °C. Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model were used to calculate the specific surface area, pore volume and pore diameter of catalysts. The transmission electron microscope (TEM) analysis was used to research the morphology images of the catalysts by JEM-2100F, JEOL microscope with an accelerating voltage of 200 kV. The surface property of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250xi, England) with $\text{Al K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). Both NH_3 -temperature programmed desorption (NH_3 -TPD) and H_2 temperature-programmed reduction (H_2 -TPR) tests were performed on the FINESORB-3010 temperature programmed adsorption instrument (Zhejiang Pantech) with using 80 mg catalysts. For NH_3 -TPD test, the catalysts were pretreated in He atmosphere at 150 °C for 1 h, and then cooled to 50 °C in the same stream. Then the input gas was shifted a 3% $\text{NH}_3 + \text{He}$ (25 mL min^{-1}) mixed atmosphere at 50 °C, and the adsorption in this atmosphere lasted for 30 minutes. Before starting the TPD experiment, the catalyst was flushed with He at a flow rate of 30 mL min^{-1} to remove physically adsorbed NH_3 on its surface. The desorption process was performed by heating the samples in He (30 mL min^{-1}) from 50 °C to 600 °C at a heating rate of 10 °C min^{-1} , the data was detected and recorded online by a thermal conductivity detector (TCD), then analyzed by the Origin software. Each desorption peak was integrated to obtain the corresponding peak area, as well as the total acid content and the ratio of strong and weak acid sites were calculated. For H_2 -TPR experiment, 80 mg catalyst (particle size: 40–60 mesh) was putted into a laboratory-made quartz tube, and pre-treated in pure Ar atmosphere (flow rate: 20 mL min^{-1}) for 1 h at 300 °C. Then cooled down the temperature to 30 °C and stabilize for a period of time, followed by changing the gas to 10% H_2/Ar , and the reduction process occurred from 30 °C to 600 °C at a heating rate of 10 °C min^{-1} . The corresponding data was detected and recorded by TCD. Origin software was employed to fit the H_2 -TPR curve through splitting the peaks, and calculate the hydrogen consumption based on the peak area. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (*In situ* DRIFTS) experiments were performed using *In situ* infrared spectrometer (Bruker TENSOR 27) from Germany, with a Pike DRIFTS sample cell and a high-precision MCT detector cooled by liquid nitrogen. At first, the sample was pretreated at 300 °C under N_2 about 10 min, and the background spectrum was collected in the same condition at the test temperature (240 °C). Then, each spectrum was recorded by subtracting the background spectrum in the range of 2000–1000 cm^{-1} . The gas flow during reaction process included: 600 ppm NO , 600 ppm NH_3 , 5 vol% O_2 , 100 ppm SO_2 , with N_2 as the balance gas. The acid sites over the samples were investigated by infrared spectroscopy of adsorbed pyridine (Py-IR) using Bruker INVENIO S from Germany. The spectra were recorded with



2 cm⁻¹ spectral resolution on a Frontier FT-IR Spectrometer at 240 °C.

2.4. SCR activity test

The NH₃-SCR performance of the catalysts (40–60 mesh) was tested over the fixed-bed quartz tube reactor. The reaction gas was set as follows: 600 ppm NO, 600 ppm NH₃, 5 vol% O₂, 100 ppm SO₂ (when used), with N₂ as the balance gas and the space velocity (GHSV) was 45 000 h⁻¹. Experimental configurations for evaluating catalytic performance were presented in Fig. S1.†

The IR flue gas analyser (MKS) was hired to detect online gas concentration and recorded the reaction data in a steady state at each temperature point (from 150–360 °C with 30 °C as an interval). NO_x conversion and N₂ selectivity were calculated by eqn (1) and (2):

$$\text{NO}_x \text{ conversion (\%)} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity (\%)} =$$

$$\frac{[\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}}} \times 100\% \quad (2)$$

In the above formula, the subscript “[X]_{in}” and “[X]_{out}” indicate the inlet and outlet concentration of gas in a steady state flow mode, respectively.

3 Results and discussion

3.1. Catalytic performance of the catalysts

3.1.1. Catalytic activity and N₂ selectivity. The deNO_x performance of CuAl composite oxide catalysts (CuAl-LDO, CuAl-LDO/TiO₂ and CuAl-TiO₂NTs) were tested from 150 °C to 360 °C, and the results are shown in Fig. 1. It can be seen from Fig. 1 that modifying CuAl-LDO catalyst by different Ti-based materials significantly improved the NH₃-SCR performance. As displayed in Fig. 1(A), the catalytic activity of CuAl-LDO catalyst was better than the CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalysts below 240 °C, the catalytic activity of CuAl-LDO/TiO₂ catalyst was better than that of the CuAl-LDO and CuAl-LDO/TiO₂NTs catalysts above 300 °C. However, at the test temperature ranges of 210–330 °C, the CuAl-LDO/TiO₂NTs catalyst showed better catalytic activity with above 80% NO_x conversion than other catalysts. As demonstrated in Fig. 1(B), the N₂ selectivity of all catalysts showed clear downward trend with increasing temperature, suggesting that the N₂ selectivity was susceptible to ammonia oxidation at high temperature. During the whole test temperature range, CuAl-LDO catalyst afforded lowest selectivity while the CuAl-LDO/TiO₂NTs presented best N₂ selectivity of more than 90% in 150–360 °C, as well as higher than 80% for CuAl-LDO/TiO₂. The results indicated that the NH₃-SCR performance of CuAl-LDO catalyst was

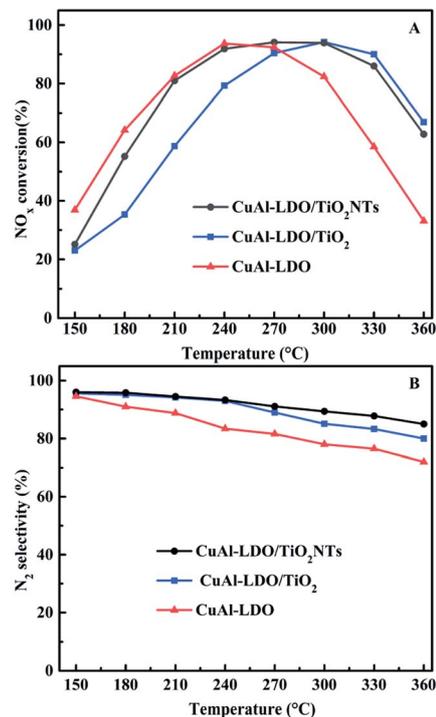


Fig. 1 The (A) NO_x conversion, (B) N₂ selectivity of catalysts.

observably affected by introducing different Ti-based materials. In addition, the stability of CuAl-LDO/TiO₂NTs catalyst was tested and results are shown in Fig. S2.† As presented, the better catalytic activity of CuAl-LDO/TiO₂NTs catalyst was kept even after seven cycle tests, indicating the superior stability.

3.1.2. The SO₂ resistance test. In NH₃-SCR reaction, the catalyst is usually deactivated by the SO₂ in the flue gas. So, the catalysts with excellent SO₂ durability are vital in practical process. Therefore, the SO₂ resistance of CuAl-LDO and CuAl-LDO/TiO₂NTs catalysts at 240 °C were tested and the corresponding results are displayed in Fig. 2. As shown in Fig. 2, after adding SO₂ into flue gas, the NO_x conversion decreased from 92% to 80% for CuAl-LDO/TiO₂NTs catalyst and 93% to 70% for

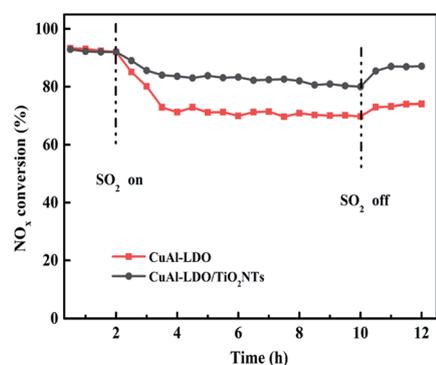


Fig. 2 SO₂ resistance test over CuAl-LDO/TiO₂NTs and CuAl-LDO catalysts at 240 °C. Reaction conditions: [NO] = [NH₃] = 600 ppm, [O₂] = 5 vol%, [SO₂] = 100 ppm, N₂ as balance gas, under a GHSV of 45 000 h⁻¹.



CuAl-LDO catalyst, respectively. After the SO₂ were purged off, the activity recovered to 86% for the CuAl-LDO/TiO₂NTs catalyst, but only 73% for CuAl-LDO catalyst. The results indicated that the CuAl-LDO/TiO₂NTs catalysts possessed better SO₂ resistance than CuAl-LDO catalyst. The capacity of SO₂ adsorption over both catalysts were researched by *In situ* DRIFTS measurement as shown in the Fig. S3.† The results displayed that the intensity of SO₂ adsorption peaks and the species of sulfate over CuAl-LDO were higher than CuAl-LDO/TiO₂NTs. As summary, it is difficult to form sulfate on the surface of CuAl-LDO/TiO₂NTs catalyst after the introduction of SO₂, which was consistent with the result of resistance SO₂ performance test.

3.2. XRD patterns and SEM images of LDHs precursors

The XRD patterns of TiO₂, TiO₂NTs (prepared by the hydrothermal method), CuAl-LDHs, CuAl-LDHs/TiO₂ and CuAl-LDHs/TiO₂NTs are presented in Fig. 3. For TiO₂ and TiO₂NTs, it could be confirmed that the diffraction peaks at 25.3°, 37.8°, 48.1°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3° and 75.1° might be assigned to the crystal planes of anatase TiO₂ phase (JCPDS # 21-1272).^{20,23} The peaks located at 11.9°, 23.8°, 34.8°, 39.1° and 60.9° in CuAl-LDHs, CuAl-LDHs/TiO₂ and CuAl-LDHs/TiO₂NTs were corresponded to the (003), (006), (012), (015) and (110) crystal planes of LDHs (JCPDS # 35-0964), respectively, indicating the successful preparation of LDHs precursors.^{18,19} For CuAl-LDHs/TiO₂NTs and CuAl-LDHs/TiO₂, the peaks around 25.28°, 36.95°,

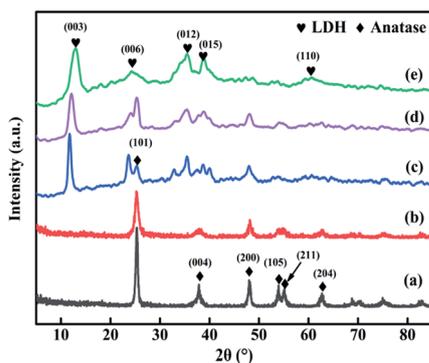


Fig. 3 The XRD patterns of (a) TiO₂(P25), (b) TiO₂NTs, (c) CuAl-LDHs/TiO₂NTs, (d) CuAl-LDHs/TiO₂ and (e) CuAl-LDHs.

37.80° and 48.05° could be ascribed to the (101), (103), (004) and (200) of anatase. The TEM images of TiO₂NTs are presented in Fig. S4(A) and (B).† The TiO₂NTs has a regular morphology and a complete hollow tubular structure.

The SEM images of CuAl-LDHs, CuAl-LDHs/TiO₂ and CuAl-LDHs/TiO₂NTs are displayed in Fig. 4. It could be seen from SEM images that all samples displayed morphology of assembled nanosheets, which was the typical structure of LDHs, thus further witnessing the successful preparation of LDHs. As shown Fig. 4(C), the nanosheets of CuAl-LDHs/TiO₂NTs were effectively separated by TiO₂NTs, which effectively alleviates the stacking and aggregation of LDHs laminates.

3.3. Characterization of the catalysts

3.3.1. XRD analysis. The XRD spectra of CuAl-LDO, CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalysts are shown in Fig. 5. As can be seen in Fig. 5, all catalysts presented the diffraction peaks of CuO (JCPDS #02-1040), while for the CuAl-LDO/TiO₂NTs catalyst, the peaks at 36.4° and 42.3° corresponding to Cu₂O crystalline phase (JCPDS # 05-0667). In addition, the diffraction peak located at 25.35° for CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalysts can be attributed to TiO₂ (JCPDS # 21-1272).

3.3.2. N₂ adsorption/desorption analysis. The N₂ adsorption-desorption isotherms and pore diameter distribution curves of CuAl-LDO, CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalysts are showed in Fig. S5.† According to Fig. S5(A),† all samples displayed isotherms of type III which exhibited hysteresis loops mostly of type H3, indicating mesoporous structure of catalysts. The pore diameter distribution curves of catalysts were calculated by the Barrett-Joyner-Halenda (BJH) model as shown in Fig. S5(B).† It can be found that the CuAl-LDO/TiO₂NTs catalyst had more abundant pore structures than others. The BET specific surface area, pore volume and pore size of different catalysts are listed in Table 1. As shown in Table 1, the specific surface area, pore volume and pore diameter of CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalysts increased in comparison to that of CuAl-LDO catalysts. Meanwhile, the specific surface area sequence of the three catalysts was CuAl-LDO/TiO₂NTs (80.5 m² g⁻¹) > CuAl-LDO/TiO₂ (51.7 m² g⁻¹) > CuAl-LDO (49.7 m² g⁻¹), hinting that the surface area of CuAl-LDO/TiO₂NTs catalyst increased more significantly. The abundant pore structures and larger surface area of CuAl-LDO/

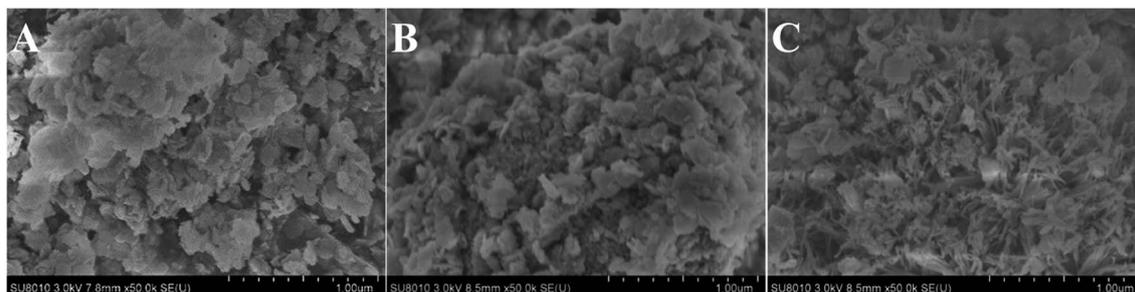


Fig. 4 The SEM images of the precursors: (A) CuAl-LDHs, (B) CuAl-LDHs/TiO₂ and (C) CuAl-LDHs/TiO₂NTs.



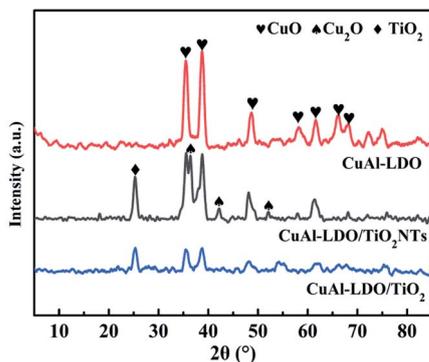


Fig. 5 The XRD patterns of catalysts.

Table 1 The specific surface area, pore volume and pore size of catalysts

Catalysts	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore diameter (nm)
CuAl-LDO	49.7	0.35	27.3
CuAl-LDO/TiO ₂	51.7	0.48	34.6
CuAl-LDO/TiO ₂ NTs	80.5	0.67	28.7
TiO ₂	55.8	0.19	14.8
TiO ₂ NTs	192.8	0.8	15.2

TiO₂NTs catalyst was not only conducive to the explosion of active centers but also beneficial to the adsorption and activation reaction gases, thus leading to the better SCR activity, being consistent with the previous literature.²⁵

3.3.3. TEM analysis. The microstructure of all catalysts was investigated by TEM tests and the results are shown in Fig. 6. It can be seen from Fig. 6(A)–(C), the thin layers still existed in CuAl-LDO, CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalyst during the annealing process. For CuAl-LDO/TiO₂NTs catalyst, it could be observed that the hollow tubular structure of TiO₂-NTs was maintained after roasting. During the LDHs annealing process, it could effectively slow down the stacking phenomenon of LDHs laminates, thereby facilitating the adsorption of reaction gas and accelerating the SCR reaction. Besides, the HR-TEM image (Fig. 6(D)) of the CuAl-LDO/TiO₂NTs presented two different lattice fringes, corresponding to the (111) crystal plane of CuO and (101) crystal plane of anatase (TiO₂), respectively. This conclusion was consistent with the results of XRD.

3.3.4. SEM & EDS-mapping analysis. The morphology and surface atomic concentration of the CuAl-LDO/TiO₂NTs catalyst were investigated by SEM and EDS-mapping analysis and the results are presented in Fig. 7. It was observed in Fig. 7(A) that the CuAl-LDO/TiO₂NTs catalyst could maintain the “flower-like” morphology after calcination. In Fig. 7(B)–(F), the EDS-mapping was applied to carry out the surface atomic concentration analysis of CuAl-LDO/TiO₂NTs catalyst. It was presented that the molar ratio of Cu/Al was about 2.8. The EDS mapping images of Cu, O, Al and Ti elements are shown in Fig. 7(C) and (D). The overlapping of all elements of Cu, O, Al and Ti verified a uniform distribution of all elements of CuAl-LDO/TiO₂NTs catalyst.

3.3.5. XPS analysis. The XPS tests were employed to study the surface element composition and electronic interaction of catalysts. The Cu 2p_{3/2}, Cu LMM XAES and O1s spectra are presented in Fig. 8, coupled with the relative calculated parameters from the fitting curves as listed in Table 2. In Fig. 8(A), the Cu 2p_{3/2} spectra at 930–937 eV of all catalysts could be divided into two peaks, corresponding to Cu²⁺ (~934 eV) and Cu⁺ (~932 eV) or Cu⁰ (~932 eV), respectively.¹⁹ The peaks at 940–945 eV of all these catalysts were attributed to the satellite peak of Cu²⁺. Usually, the binding energy of Cu⁰ was similar to that of Cu⁺, thus the Cu LMM XAES spectrums were tested to distinguish them as displayed in Fig. 8(B).²⁶ It can be seen from Fig. 8(B) that all catalysts presented the peaks located at 912–914 eV and 917 eV, which could be assigned to Cu⁺ (912–914 eV) and Cu²⁺ (917 eV). In addition, the CuAl-LDO/TiO₂NTs catalyst showed the peak at ~921 eV, contributing to the characteristics of Cu⁰.¹⁸ Meanwhile, the relative intensity of Cu⁺/(Cu²⁺ + Cu⁺) was calculated as demonstrated in Table 2, with the following order: CuAl-LDO (38.4%) > CuAl-LDO/TiO₂NTs (33.4%) > CuAl-LDO/TiO₂ (24.1%). Therefore, the synergistic effect between Cu⁺ and Cu²⁺ seems to be the main reason for the good deNO_x performance at low temperature range.

The O 1s spectra of the CuAl-LDO, CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalysts are showed in Fig. 8(C). As displayed in Fig. 8(C), the peaks at 530 eV could be assigned to the lattice oxygen species (denoted as O_I), accompanied by the chemisorbed oxygen species (denoted as O_{II}) located at 532 eV, which was closely related with the number of surface oxygen vacancies and defects of catalyst. Moreover, the peak at 533 eV for CuAl-LDO catalyst was corresponded to the adsorbed molecular water (denoted as O_{III}).^{27,28} Besides, due to the high mobility ratio, O_{II} species were beneficial to the NO → NO₂ process and favored to the “fast SCR” reaction, thus resulting in the enhancement of low temperature SCR activity.⁸ As listed in Table 2, the relative concentrations of O_{II}/(O_I + O_{II}) for CuAl-LDO/TiO₂NTs (65.2%) was higher than CuAl-LDO (54.4%) and CuAl-LDO/TiO₂ (62.3%). It could be concluded that the CuAl-LDO/TiO₂NTs owned more abundant surface oxygen than CuAl-LDO and CuAl-LDO/TiO₂, which might be helpful to the improvement of catalytic activity.

3.3.6. H₂-TPR analysis. The redox ability of catalysts is closely related to the NH₃-SCR performance, thus the H₂-TPR technique has been widely used and the results are showed in Fig. 9. Meanwhile, the reduction peak temperature and H₂ consumption of each catalyst are listed in Table 3. Two reduction peaks could be observed over TPR profiles for all catalysts. The first peak at 190 °C (CuAl-LDO), 224 °C (CuAl-LDO/TiO₂NTs) and 285 °C (CuAl-LDO/TiO₂) might be assigned to the reduction of highly dispersed CuO particles, being related to the reduction of Cu²⁺ → Cu⁺ → Cu.^{29,30} While the second peak located at 240 °C (CuAl-LDO), 271 °C (CuAl-LDO/TiO₂NTs) and 327 °C (CuAl-LDO/TiO₂) could be attributed to the reduction of the small crystalline CuO, the results above are consistent with the XRD results in Fig. 5.³⁰ As presented in Fig. 9(A), both peaks for CuAl-LDO/TiO₂NTs catalyst shifted to lower temperature comparing with CuAl-LDO/TiO₂, indicating the better reduction



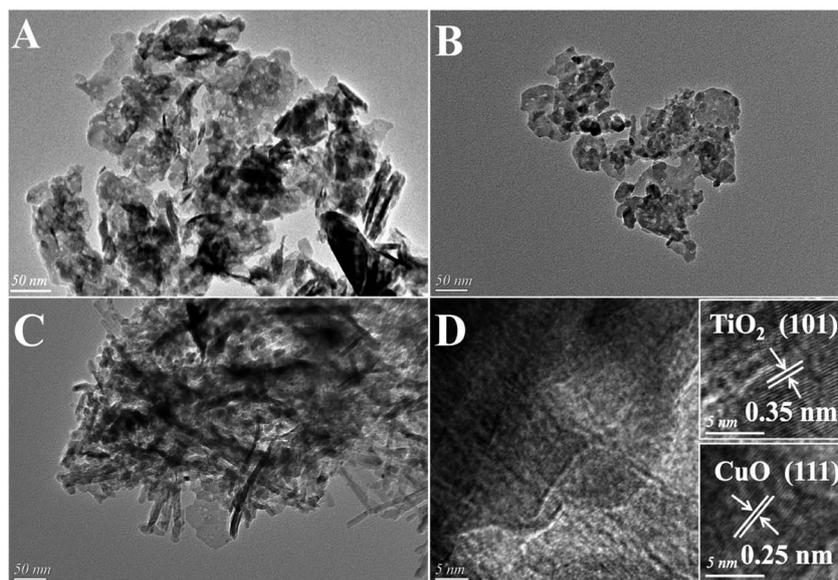


Fig. 6 The (A–C) TEM and (D) HR-TEM images of catalysts: (A) CuAl-LDO, (B) CuAl-LDO/TiO₂ and (C and D) CuAl-LDO/TiO₂NTs.

ability of the former one, which might be profited from the property of TiO₂NTs further resulting in the higher NO_x conversion of CuAl-LDO/TiO₂NTs catalyst at low temperature. It

was noteworthy that the reduction temperature of CuAl-LDO/TiO₂NTs catalyst was slightly higher than CuAl-LDO, which was consistent with the results of low temperature NH₃-SCR activity.

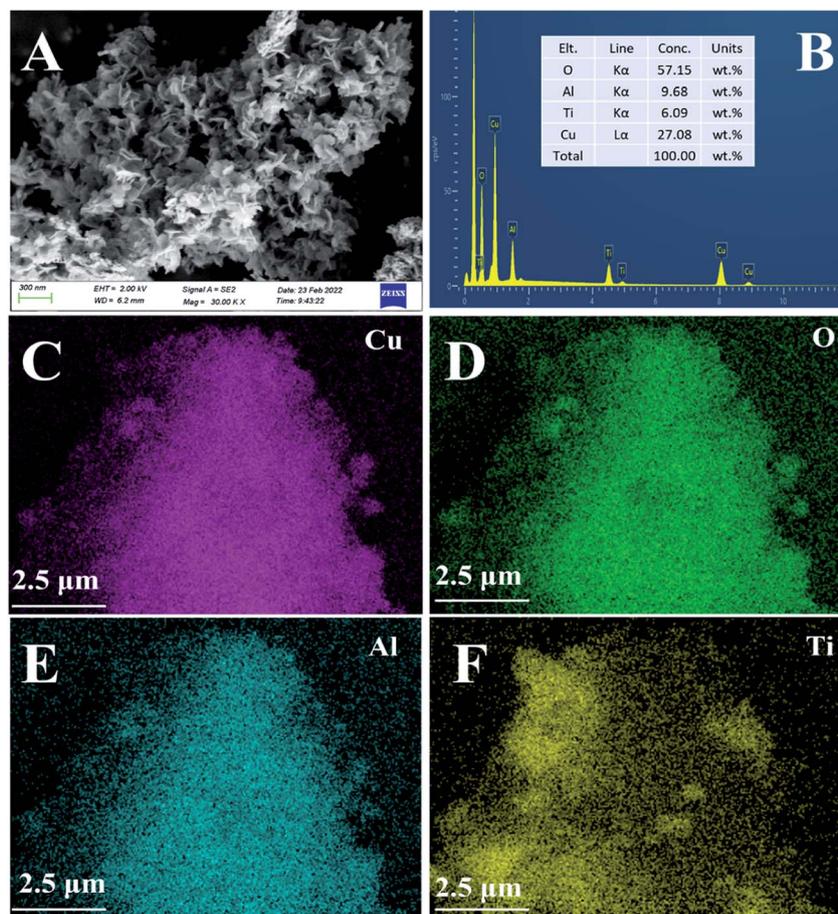


Fig. 7 The (A) SEM images and (B–F) EDS-mapping of CuAl-LDO/TiO₂NTs catalyst: (C) Cu, (D) O, (E) Al and (F) Ti.



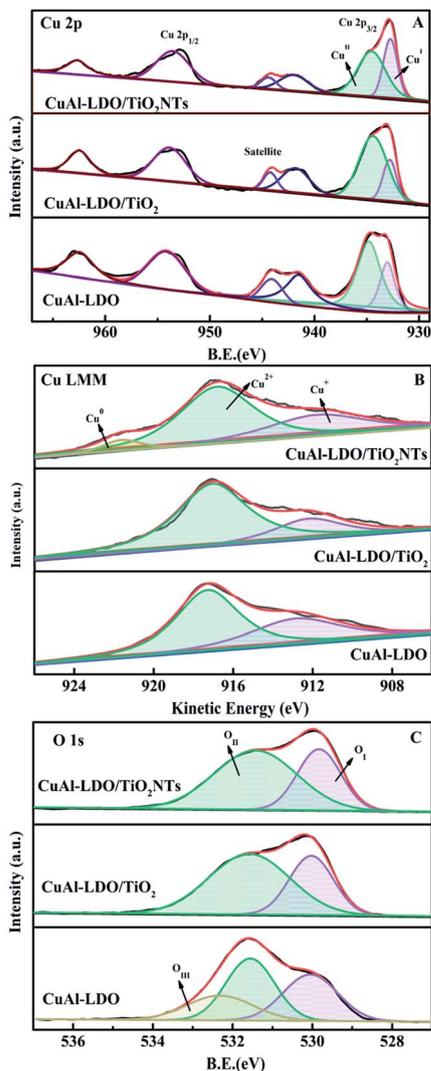


Fig. 8 The XPS spectra of the CuAl-LDO, CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalysts: (A) Cu 2p, (B) Cu LMM XAES, and (C) O 1s.

Table 2 The surface components of catalysts obtained by XPS analysis

Catalysts	Cu LMM XAES kinetic energy (eV)			Relative concentration ratio/%	
	Cu ⁺	Cu ²⁺	Cu ⁰	Cu ⁺ /(Cu ²⁺ + Cu ⁺) ^a	O _{II} /(O _I + O _{II})
CuAl-LDO	913.0	917.4	—	38.4	54.4
CuAl-LDO/TiO ₂	914.0	917.2	920.6	24.1	62.3
CuAl-LDO/TiO ₂ NTs	913.1	917.0	921.4	33.7	65.2

^a Intensity ratio between Cu⁺ and (Cu⁺ + Cu²⁺) by deconvolution of Cu LMM XAES spectra.

Moreover, the calculated results shown in Table 3 further illuminating that the CuAl-LDO/TiO₂NTs catalyst with higher H₂ consumption was more favorable for the redox reaction.

3.3.7. NH₃-TPD analysis. In addition to redox ability, the acidity of catalyst was also the main factor for SCR activity. The NH₃-TPD profiles of CuAl-LDO, CuAl-LDO/TiO₂ and CuAl-LDO/

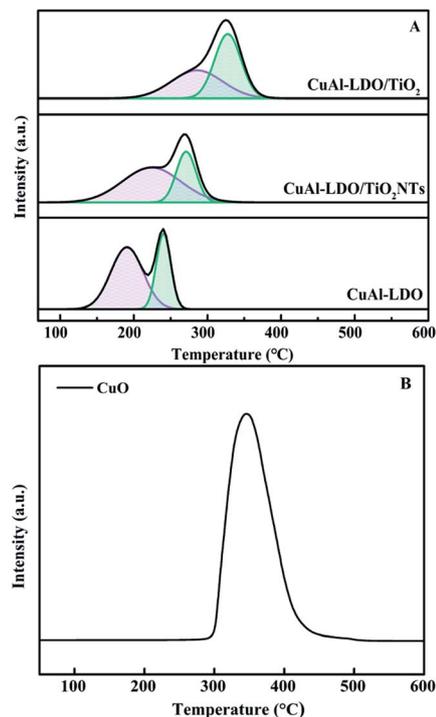


Fig. 9 The H₂-TPR profiles of (A) catalysts and (B) CuO standard sample.

TiO₂NTs catalysts are shown in Fig. 10, which researched the quantity and intensity of acidity over the catalyst surface. The relative acid contents of the catalysts calculated by normalizing the area of the NH₃ desorption peak of CuAl-LDO catalyst are listed in Table 3. It can be seen from the Fig. 10 that the CuAl-LDO catalyst showed a larger NH₃ desorption peak at 140 °C, indicating the existence of more weak acid sites. Compared with CuAl-LDO catalyst, the CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂NTs catalysts presented significantly desorption peaks near 300 °C and 270 °C, respectively, which contributed to the medium-strong acid sites. While the small desorption peak located at around 530 °C for three catalysts could be assigned to the ammonia desorption from strong acid sites. As summarized in Table 3, the total amount of acid sites over CuAl-LDO/TiO₂NTs catalyst was richer than CuAl-LDO and CuAl-LDO/TiO₂ catalysts, which could be attributed to the outstanding catalytic performance of the CuAl-LDO/TiO₂NTs catalyst in the total test temperature range.³¹

3.3.8. Py-IR analysis. The properties of acid species on the surface of CuAl-LDO and CuAl-LDO/TiO₂NTs catalysts were investigated by Pyridine Adsorption Fourier-transform Infrared (Py-IR) and the results are presented in Fig. 11. For CuAl-LDO and CuAl-LDO/TiO₂NTs catalysts, both the Brønsted and Lewis acid sites were detected simultaneously over the surface. The bands located at ~1440 cm⁻¹, ~1540 cm⁻¹, 1590 cm⁻¹ and 1655 cm⁻¹ were corresponded to the Lewis acid sites (~1440 cm⁻¹ and 1590 cm⁻¹) and Brønsted acid sites (~1540 cm⁻¹ and 1655 cm⁻¹), respectively.^{32,33} The bands around 1485 cm⁻¹ were assigned to both Brønsted and Lewis



Table 3 The reduction peak attribution, amount of hydrogen consumption and normalized NH₃ desorption amount of catalysts

Catalysts	Reduction temperature (°C)		H ₂ consumption ^a (mmol g ⁻¹)	Total amount of NH ₃ desorption ^b
	T ₁	T ₂		
CuAl-LDO	190	240	1.3	1
CuAl-LDO/TiO ₂	285	327	1.4	1.7
CuAl-LDO/TiO ₂ NTs	224	271	1.5	2.7

^a The H₂ consumption of catalysts was calculated with CuO standard sample. ^b Normalized by the NH₃ total desorption peak area of CuAl-LDO.

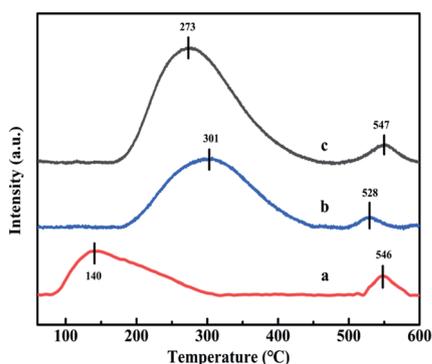


Fig. 10 The NH₃-TPD profiles of catalysts: (a) CuAl-LDO, (b) CuAl-LDO/TiO₂ and (c) CuAl-LDO/TiO₂NTs.

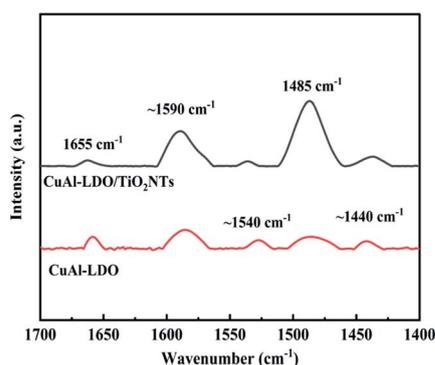


Fig. 11 Py-IR spectra of CuAl-LDO catalyst and CuAl-LDO/TiO₂NTs catalyst.

acid sites over catalysts.³⁴ The literature was reported that there was only Lewis acid sites over the anatase (TiO₂).^{32,33,35} Therefore, the intensity of the band of the Lewis acid sites over CuAl-LDO/TiO₂NTs catalyst was stronger than CuAl-LDO catalyst. In addition, compared with CuAl-LDO, CuAl-LDO/TiO₂NTs catalyst have the most abundant and strongest acid sites over the surface, which was in good agreement with their NH₃-TPD results.

3.4. *In situ* DRIFTS analysis

3.4.1. Adsorption of NH₃. The capacity of NH₃ adsorption over CuAl-LDO and CuAl-LDO/TiO₂NTs catalysts were studied by *In situ* DRIFTS measurement. As shown in Fig. 12(a), for

CuAl-LDO catalyst, the bands appeared at 1770–1640 cm⁻¹, 1458 cm⁻¹ and 1421 cm⁻¹ could be assigned to NH₄⁺ species on Brønsted acid sites.^{36,37} The peaks of coordinated NH₃ linked to Lewis acid sites were observed at 1621 cm⁻¹, 1543 cm⁻¹ and 1228 cm⁻¹.³⁸ And the bands located at 1513 cm⁻¹ and 1390 cm⁻¹ were attributed to the –NH₂ scissoring and wagging of N₂H₄ species, separately.^{16,39} The peaks for CuAl-LDO/TiO₂NTs catalyst (in Fig. 12(b)) at 1692 cm⁻¹, 1620 cm⁻¹, 1545 cm⁻¹, 1517 cm⁻¹, 1461 cm⁻¹, 1422 cm⁻¹, 1393 cm⁻¹ and 1218 cm⁻¹ could be correspondingly assigned to the symmetric and asymmetric vibration of NH₃ species adsorbed on Lewis acid sites (1620 cm⁻¹, 1545 cm⁻¹ and 1218 cm⁻¹), the –NH₂ scissoring and wagging of N₂H₄ species (1517 cm⁻¹ and 1393 cm⁻¹) and NH₄⁺ ions bounded on Brønsted acid site (1692 cm⁻¹, 1461 cm⁻¹ and 1422 cm⁻¹).^{16,38,40} It could be concluded that the Lewis acid sites and Brønsted acid sites coexisted on the surface of both catalysts. In Fig. 12, it could be found that the peak

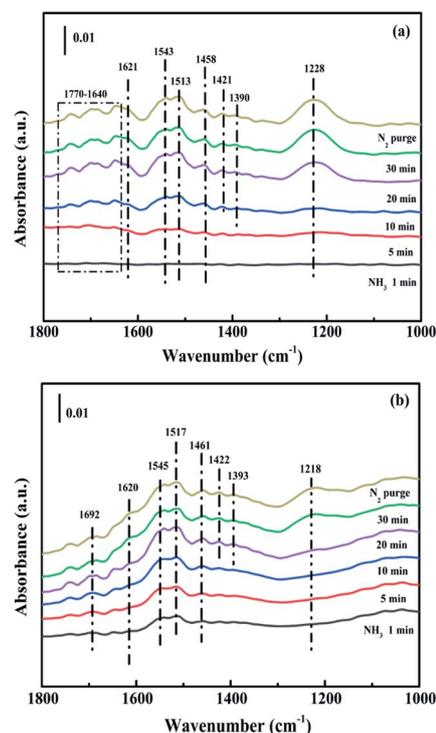


Fig. 12 *In situ* DRIFTS spectra of NH₃ adsorption at 240 °C over (a) CuAl-LDO and (b) CuAl-LDO/TiO₂NTs catalysts.



intensity of the bands assigned to Brønsted acid sites and Lewis acid sites of CuAl-LDO/TiO₂NTs catalyst was higher than that of the CuAl-LDO catalyst, indicating the better NH₃ adsorption capacity of CuAl-LDO/TiO₂NTs catalyst.¹³

3.4.2. Co-adsorption of NO and O₂. *In situ* DRIFTS experiments of NO + O₂ adsorption were applied to research the formation and transformation of NO_x species over the CuAl-LDO and CuAl-LDO/TiO₂NTs catalysts. In Fig. 13(a), the bands at 1271 cm⁻¹, 1240 cm⁻¹ and 1135 cm⁻¹ were detected for CuAl-LDO catalyst, which could be ascribed to linear nitrite (1454 cm⁻¹), monodentate nitrite (1271 cm⁻¹ and 1135 cm⁻¹) and bridged nitrate (1240 cm⁻¹), respectively.^{36,41} For CuAl-LDO/TiO₂NTs catalyst, the bands located at 1745–1700 cm⁻¹, 1646 cm⁻¹, 1547 cm⁻¹, 1516 cm⁻¹, 1455 cm⁻¹, 1424 cm⁻¹, 1393 cm⁻¹, 1232 cm⁻¹ and 1108 cm⁻¹ could be assigned to the absorbed N₂O₄ (1745–1700 cm⁻¹), bridged nitrate (1646 cm⁻¹ and 1232 cm⁻¹), bidentate nitrate (1547 cm⁻¹ and 1516 cm⁻¹), linear nitrite (1455 cm⁻¹), monodentate nitrite (1424 cm⁻¹, 1393 cm⁻¹ and 1108 cm⁻¹).^{16,36,41,42} The intensity of peak located at 1232 cm⁻¹ was gradually decreased along with the appearance of the band of monodentate nitrate (1262 cm⁻¹). The results displayed that the intensity of NO_x adsorbed peaks over CuAl-LDO/TiO₂NTs were higher than CuAl-LDO. It could be concluded that there was larger amount of NO adsorbed on the CuAl-LDO/TiO₂NTs catalyst surface and oxidized to a variety of nitrate species, which resulting in the excellent SCR performance.

3.4.3. Reaction between nitrogen oxides and ammonia species. In order to explore the potential reaction species and possible pathway, the transient reactions between NH₃ and NO + O₂ over CuAl-LDO and CuAl-LDO/TiO₂NTs catalysts were

further carried out at 240 °C. As shown in Fig. 14(a), the CuAl-LDO catalyst was firstly absorbed with NH₃ for 30 min. The peaks located at 1770–1640 cm⁻¹, 1458 cm⁻¹ and 1421 cm⁻¹ (NH₄⁺ species on Brønsted acid sites), 1621 cm⁻¹, 1543 cm⁻¹ and 1228 cm⁻¹ (NH₃ linked to Lewis acid sites) and 1513 cm⁻¹ and 1390 cm⁻¹ (–NH₂ scissoring and wagging of N₂H₄ species) were detected.^{16,36,38,39,43} After inletting NO + O₂ for 10 min, except for the peak located at 1228 cm⁻¹, other peaks almost disappeared, might propose the reaction between adsorbed NH₃ species and NO_x species. After imported NO + O₂ for 20 min, the news bands located at 1721 cm⁻¹, 1667 cm⁻¹, 1621 cm⁻¹, 1596 cm⁻¹, 1484 cm⁻¹, 1440 cm⁻¹ and 1136 cm⁻¹ appeared which could be assigned to the absorbed N₂O₄ (1721 cm⁻¹), bridged nitrate (1667 cm⁻¹), gaseous NO₂ (1621 cm⁻¹), bidentate nitrate (1596 cm⁻¹), linear nitrite (1440 cm⁻¹), monodentate nitrate (1484 cm⁻¹ and 1136 cm⁻¹), respectively.^{16,25,36,42} When the reactant gases were introduced as reverse order, the corresponding results are displayed in Fig. 14(c). As can be seen, the pre-adsorption of NO + O₂ lead to the formation of linear nitrite (1454 cm⁻¹), monodentate nitrite (1271 cm⁻¹ and 1135 cm⁻¹) and bridged nitrate (1240 cm⁻¹), respectively. The further introduction of NH₃ caused the generation of peaks located at 1770–1640 cm⁻¹, 1458 cm⁻¹ and 1421 cm⁻¹ (NH₄⁺ species on Brønsted acid sites), 1621 cm⁻¹, 1543 cm⁻¹ and 1228 cm⁻¹ (coordinated NH₃ linked to Lewis acid sites) and 1513 cm⁻¹ (–NH₂ scissoring of N₂H₄ species) were detected.^{41,44,45} It was worth noting that the intensity of peak located at 1240 cm⁻¹ ascribed to bridged nitrite further increased after introducing NH₃, which might be due to the coverage of coordinated NH₃ linked to Lewis acid sites (1228 cm⁻¹). The results indicated that the Eley–Rideal (E–R) mechanisms and Langmuir–Hinshelwood (L–H) mechanisms were occurred simultaneously over the surface of CuAl-LDO catalysts at 240 °C, and the E–R mechanisms were the main reaction way.

While for CuAl-LDO/TiO₂NTs catalysts, the transient reaction spectra are displayed in Fig. 14(b) and (d). After pre-adsorption of NH₃, the following bands emerged, NH₄⁺ ions bounded on Brønsted acid site (1692 cm⁻¹, 1461 cm⁻¹ and 1422 cm⁻¹), the symmetric and asymmetric vibration of NH₃ species adsorbed on Lewis acid sites (1620 cm⁻¹, 1545 cm⁻¹ and 1218 cm⁻¹), the –NH₂ scissoring and wagging of N₂H₄ species (1517 cm⁻¹ and 1393 cm⁻¹).^{16,39,46} Further importing NO + O₂, the intensity of all peaks gradually impaired, replaced by the arising of peak located at 1237 cm⁻¹ corresponding to monodentate nitrate species. In comparison with the Fig. 13(b), there was no significant accumulation of nitrate species participating in the NH₃-SCR reaction. When the reactant gases were introduced as the inverse order, the results are presented in Fig. 14(d). While NO + O₂ were imported for 30 min, the corresponding species appeared as follows: the absorbed N₂O₄ (1745–1700 cm⁻¹), bridged nitrate (1646 cm⁻¹ and 1232 cm⁻¹), bidentate nitrate (1547 cm⁻¹ and 1516 cm⁻¹), linear nitrite (1455 cm⁻¹), monodentate nitrite (1424 cm⁻¹, 1393 cm⁻¹ and 1108 cm⁻¹), monodentate nitrate (1262 cm⁻¹).^{16,25,42,47} With an increase in the adsorption time of NH₃, the bands of NO_x species gradually reduced (1745–1700 cm⁻¹, 1646 cm⁻¹,

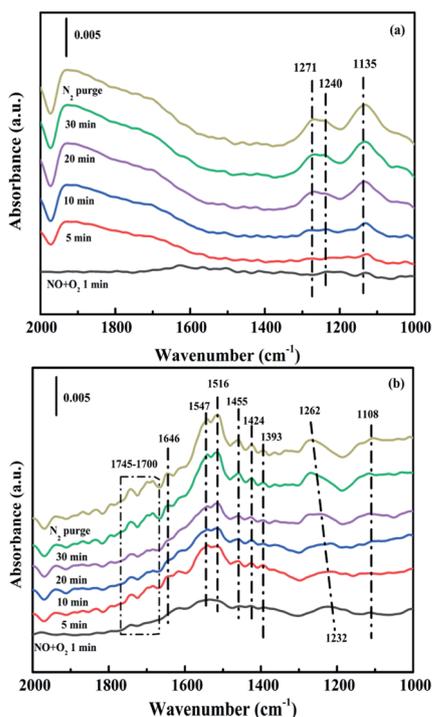


Fig. 13 *In situ* DRIFTS spectra of NO + O₂ adsorption at 240 °C over (a) CuAl-LDO and (b) CuAl-LDO/TiO₂NTs catalyst.



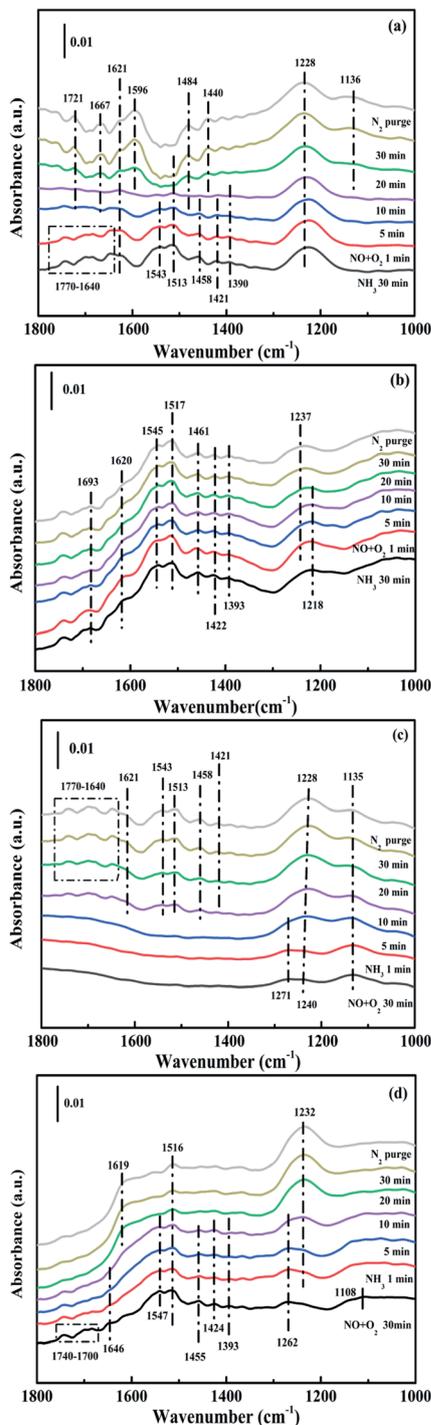


Fig. 14 *In situ* DRIFTS spectra of (a and b) NO + O₂ adsorption with pre-absorbed NH₃ and (c and d) NH₃ adsorption with pre-absorbed NO + O₂ at 240 °C over (a and c) CuAl-LDO and (b and d) CuAl-LDO/TiO₂NTs catalysts.

1547 cm⁻¹, 1455 cm⁻¹, 1424 cm⁻¹, 1393 cm⁻¹, 1262 cm⁻¹ and 1108 cm⁻¹), accompanied by the emergence of bands located at 1619 cm⁻¹ and 1232 cm⁻¹, which were consistent with the asymmetric and symmetric bending vibrations of NH₃ adsorbed on Lewis acid sites (1619 cm⁻¹ and 1232 cm⁻¹).^{13,48}

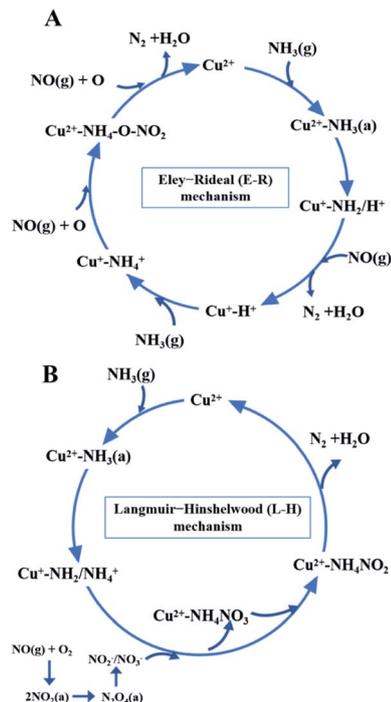


Fig. 15 The NH₃-SCR reaction mechanisms over CuAl-LDO/TiO₂NTs catalyst.

Consequently, the NH₃ species adsorbed on the Lewis acid sites could react with nitrate and nitrite species on the surface of CuAl-LDO/TiO₂NTs catalyst in the SCR reaction. The results indicated that CuAl-LDO/TiO₂NTs catalysed the SCR reaction in both E-R mechanism and L-H mechanism. Based on *In situ* DRIFTS, the reaction mechanisms for CuAl-LDO/TiO₂NTs catalyst were proposed, which was displayed in Fig. 15.

4 Conclusions

In summary, CuAl-LDO, CuAl-LDO/TiO₂ and CuAl-LDO/TiO₂-NTs catalysts were obtained by calcining the LDHs precursor, and then applied in NH₃-SCR reaction. The results demonstrated that the introduction of TiO₂NTs with hollow tubular structure effectively avoided the stacking and accumulation of laminates during calcination process and enhanced the number of acidic sites on the catalyst. Consequently, the CuAl-LDO/TiO₂NTs catalyst showed excellent NO_x conversion, N₂ selectivity as well as the good SO₂ resistance. XRD results illustrated that a new phase of Cu₂O was formed in the CuAl-LDO/TiO₂NTs catalyst. Other characterization results indicated that the excellent deNO_x performance of the CuAl-LDO/TiO₂NTs catalyst depended on the synergistic effect between CuO and Cu₂O, which could contribute to the larger surface area, more acidic sites, better redox performance, more abundant surface chemisorption oxygen species and stronger adsorption capacity of reactant gases. This work presents the preparation of Cu-based catalysts with wide temperature window *via* modifying LDHs template, which might serve as an important reference for LDHs precursor to be tailored in NH₃-SCR filed.



Author contributions

Yali Du: validation, formal analysis, writing – review & editing, funding acquisition. Xuezhen Liu: methodology, formal analysis, investigation, resources, data curation, writing – original draft. Jiangning Liu: writing – review & editing, formal analysis. Rongting Du: writing – review & editing. Xu Wu: conceptualization, funding acquisition, project administration, supervision.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51978436), the National Natural Science Foundation of China (52000092), the Natural Science Foundation of Shanxi Province, China (201901D211445) and China Postdoctoral Science Foundation (2020M670706).

References

- D. Damma, P. Ettireddy, B. Reddy and P. Smirniotis, *Catalysts*, 2019, **9**, 349.
- V. Praveena and M. L. J. Martin, *J. Energy Inst.*, 2018, **91**, 704–720.
- M. Fu, C. Li, P. Lu, L. Qu, M. Zhang, Y. Zhou, M. Yu and Y. Fang, *Catal. Sci. Technol.*, 2014, **4**, 14–25.
- Q. Yan, S. Chen, L. Qiu, Y. Gao, D. O'Hare and Q. Wang, *Dalton Trans.*, 2018, **47**, 2992–3004.
- W. Wang, Z. Xiong, W. He, W. Lu and H. Shi, *J. Energy Inst.*, 2021, **98**, 322–333.
- C. Chen, Y. Cao, S. Liu, J. Chen and W. Jia, *Chin. J. Catal.*, 2018, **39**, 1347–1365.
- Z. Song, Y. Xing, X. Zhang, H. Zhao, M. Zhao, J. Zhao, Z. Ma and Q. Zhang, *Appl. Organomet. Chem.*, 2019, **33**, e5160.
- C. Li, Z. Xiong, Y. Du, X. Ning, Z. Li, J. He, X. Qu, W. Lu, S. Wu and L. Tan, *J. Energy Inst.*, 2020, **93**, 1809–1818.
- S. Zang, G. Zhang, W. Qiu, L. Song, R. Zhang and H. He, *Chin. J. Catal.*, 2016, **37**, 888–897.
- Z. Fan, J.-W. Shi, C. Gao, G. Gao, B. Wang, Y. Wang, C. He and C. Niu, *Chem. Eng. J.*, 2018, **348**, 820–830.
- K. Cheng, W. Song, Y. Cheng, H. Zheng, L. Wang, J. Liu, Z. Zhao and Y. Wei, *RSC Adv.*, 2018, **8**, 19301–19309.
- B. Hou, Y. Du, X. Liu, C. Ci, X. Wu and X. Xie, *RSC Adv.*, 2019, **9**, 24377–24385.
- S. Ali, L. Chen, Z. Li, T. Zhang, R. Li, S. H. Bakhtiar, X. Leng, F. Yuan, X. Niu and Y. Zhu, *Appl. Catal. B Environ.*, 2018, **236**, 25–35.
- X. Gao, X. Du, L. Cui, Y. Fu, Z. Luo and K. Cen, *Catal. Commun.*, 2010, **12**, 255–258.
- S. Suárez, J. A. Martín, M. Yates, P. Avila and J. Blanco, *J. Catal.*, 2005, **229**, 227–236.
- X. Yao, L. Zhang, L. Li, L. Liu, Y. Cao, X. Dong, F. Gao, Y. Deng, C. Tang, Z. Chen, L. Dong and Y. Chen, *Appl. Catal. B Environ.*, 2014, **150–151**, 315–329.
- X. Wu, R. Wang, Y. Du, C. Zou, H. Meng and X. Xie, *Mol. Catal.*, 2019, **467**, 150–160.
- X. Wu, H. Meng, Y. Du, J. Liu, B. Hou and X. Xie, *J. Catal.*, 2020, **384**, 72–87.
- Q. Yan, Y. Nie, R. Yang, Y. Cui, D. O'Hare and Q. Wang, *Appl. Catal. Gen.*, 2017, **538**, 37–50.
- R. Fan, Z. Li, Y. Wang, C. Zhang, Y. Wang, Z. Ding, X. Guo and R. Wang, *RSC Adv.*, 2020, **10**, 5845–5852.
- D. K. Pappas, T. Boningari, P. Boolchand and P. G. Smirniotis, *J. Catal.*, 2016, **334**, 1–13.
- S.-A. Chen, J.-N. Nian, C.-C. Tsai and H. Teng, *J. Air Waste Manage. Assoc.*, 2007, **57**, 600–605.
- Z. Cai, G. Zhang, Z. Tang and J. Zhang, *ACS Appl. Nano Mater.*, 2021, **4**, 6201–6211.
- C. Liu, L. Chen, J. Li, L. Ma, H. Arandiyani, Y. Du, J. Xu and J. Hao, *Environ. Sci. Technol.*, 2012, **46**, 6182–6189.
- D. Meng, W. Zhan, Y. Guo, Y. Guo, L. Wang and G. Lu, *ACS Catal.*, 2015, **5**, 5973–5983.
- Z. He, H. Lin, P. He and Y. Yuan, *J. Catal.*, 2011, **277**, 54–63.
- L. Dou, T. Fan and H. Zhang, *Catal. Sci. Technol.*, 2015, **5**, 5153–5167.
- Y. Geng, W. Shan, F. Liu and S. Yang, *J. Hazard. Mater.*, 2021, **405**, 124223.
- M. Ma, R. Yang, Z. Jiang, C. Chen, Q. Liu, R. Albilali and C. He, *Fuel*, 2021, **303**, 121244.
- Q. Yan, Y. Gao, Y. Li, M. A. Vasiliades, S. Chen, C. Zhang, R. Gui, Q. Wang, T. Zhu and A. M. Efstathiou, *Appl. Catal. B Environ.*, 2019, **255**, 117749.
- J. Zhang, H. Tian, Y. Yu, Z. Jiang, M. Ma and C. He, *Catal. Lett.*, 2021, **151**, 2502–2512.
- Y. Liu, Y. Guan, C. Li, J. Lian, G. Gan, E. Lim and F. Kooli, *J. Catal.*, 2006, **244**, 17–23.
- L. Sun, S. Cao, Y. Huang, Y. Zhang, Y. Xiao, G. Dong and Y. Su, *RSC Adv.*, 2019, **9**, 30340–30349.
- W. Yao, Y. Liu, X. Wang, X. Weng, H. Wang and Z. Wu, *J. Phys. Chem. C*, 2016, **120**, 221–229.
- L. Li, H. Yue, T. Ji, W. Li, X. Zhao, L. Wang, J. She, X. Gu and X. Li, *Appl. Catal. Gen.*, 2019, **574**, 25–32.
- L. Chen, Z. Si, X. Wu and D. Weng, *ACS Appl. Mater. Interfaces*, 2014, **6**, 8134–8145.
- Q. Zhang, T. Zhang, F. Xia, Y. Zhang, H. Wang and P. Ning, *Appl. Surf. Sci.*, 2020, **500**, 144044.
- J. Ma, Y. Li, J. Liu, Z. Zhao, C. Xu, Y. Wei, W. Song, Y. Sun and X. Zhang, *Ind. Eng. Chem. Res.*, 2019, **58**, 2389–2395.
- C. Yu, B. Huang, L. Dong, F. Chen and X. Liu, *Catal. Today*, 2017, **281**, 610–620.
- Y. Wei, P. Zhang, J. Xiong, Q. Yu, Q. Wu, Z. Zhao and J. Liu, *Environ. Sci. Technol.*, 2020, **54**, 6947–6956.
- H. Hu, S. Cai, H. Li, L. Huang, L. Shi and D. Zhang, *J. Phys. Chem. C*, 2015, **119**, 22924–22933.
- G. Zhou, B. Zhong, W. Wang, X. Guan, B. Huang, D. Ye and H. Wu, *Catal. Today*, 2011, **175**, 157–163.
- T. Zhang, R. Qu, W. Su and J. Li, *Appl. Catal. B Environ.*, 2015, **176–177**, 338–346.



Paper

- 44 L. Wei, S. Cui, H. Guo, X. Ma and L. Zhang, *J. Mol. Catal. Chem.*, 2016, **421**, 102–108.
- 45 Z. Zhang, L. Chen, Z. Li, P. Li, F. Yuan, X. Niu and Y. Zhu, *Catal. Sci. Technol.*, 2016, **6**, 7151–7162.
- 46 R. Gao, D. Zhang, X. Liu, L. Shi, P. Maitarad, H. Li, J. Zhang and W. Cao, *Catal. Sci. Technol.*, 2013, **3**, 191–199.
- 47 Y. Wen, S. Cao, X. Fei, H. Wang and Z. Wu, *Chin. J. Catal.*, 2018, **39**, 771–778.
- 48 Z. Liu, H. Liu, X. Feng, L. Ma, X. Cao and B. Wang, *Mol. Catal.*, 2018, **445**, 179–186.

