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# The catalytic performances and reaction mechanism of nanoparticle Cd/Ce–Ti oxide catalysts for NH<sub>3</sub>-SCR reaction†

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Ce<sub>0.3</sub>–TiO<sub>x</sub> nanoparticle carrier was prepared by the sol–gel method, and a series of Cd–Ce–Ti nanoparticle catalysts with variable Cd contents were prepared by the means of an improved incipient-wetness impregnation. The catalysts were characterized by means of XRD, N<sub>2</sub> adsorption–desorption analysis, SEM, TEM, NH<sub>3</sub>-TPD and *in situ* DRIFTS. The catalytic activities for deNO<sub>x</sub> were evaluated by NH<sub>3</sub>-SCR reaction. All these nanoparticle catalysts contain mesopores with a pore size around 7 nm, and the average particle size is 20 nm. Among the catalysts, 2 wt% Cd/Ce<sub>0.3</sub>TiO<sub>x</sub> catalyst exhibits the best NH<sub>3</sub>-SCR performance with a wide temperature window of 250–400 °C for NO conversion above 90%. Moreover, *in situ* DRIFTS spectra of NO<sub>x</sub> reduction over 2 wt% Cd/Ce<sub>0.3</sub>TiO<sub>x</sub> catalyst were also investigated. The results show that this reaction mainly follows the Langmuir–Hinshelwood mechanism at room temperature, while Eley–Rideal mechanism plays more important role when the reaction temperature is higher than 150 °C. The adsorbed NH<sub>3</sub> coordinately linked to Lewis acid site is easy to react with NO<sub>x</sub> at high temperature.

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## 1. Introduction

It is generally considered that the air pollution is predominantly from 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 known as major causes of photochemical smog, haze, acid rain, ozone depletion and the greenhouse effect.<sup>1,2</sup> 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.<sup>3–5</sup> 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.<sup>6,7</sup> 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 SCR atmosphere such as H<sub>2</sub>O, SO<sub>2</sub> or alkali metals *etc.*<sup>8–10</sup>

In recent years, Ce–Ti based catalysts for NH<sub>3</sub>-SCR reaction have been attracted much attention from researchers. This kind of catalyst indeed offers a number of advantages over V–Ti catalysts. They are active and selective in a wider temperature range, nontoxic, and high N<sub>2</sub> selectivity even at high temperatures.<sup>11–14</sup> The transition metal Cd, is belong to IIB elements, and has attracted attention in environmental catalysis, photocatalysis and hydrodesulfurization.<sup>15,16</sup> However, there is lack to study for NO<sub>x</sub> reduction. By the incorporation of metal oxide Cd into the ceria lattice, it is beneficial to the formation of mixed oxides or solid solutions.

In this work, Cd<sub>M</sub>/Ce<sub>0.3</sub>–TiO<sub>x</sub> nanoparticle catalysts were prepared by the incipient-wetness impregnation method with different Cd contents for improving the catalytic performances for the SCR of NO with NH<sub>3</sub>. Their physicochemical properties were investigated systematically.

## 2. Experimental

### 2.1 Catalyst preparation

Ce<sub>0.3</sub>–TiO<sub>2</sub> nanoparticle carrier was prepared by the sol–gel method. All chemicals were of analytical grade. A solution of deionized water (2 ml), anhydrous ethanol (10 ml) and a certain amount of cerium nitrate were vigorously stirred at room temperature. The solution was added dropwise into the mixing solution of butyl titanate (10 g) and anhydrous ethanol (30 ml), and then a certain amount of hydrochloric acid was added to adjust pH until pH = 1. The obtained mixture was stirred for 4 h

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and placed at room temperature for about 2 days to form a gelatum. Then the gelatum was dried at 100 °C for 24 h and calcined at 500 °C for 4 h in air. The sample is denoted as  $\text{Ce}_{0.3}\text{TiO}_x$ , where the molar ratio of Ce and Ti is 0.3 : 1.

A series of  $\text{Cd}_M/\text{Ce}_{0.3}\text{TiO}_x$  ( $M = 1, 2, 3, 5$ , wt%) nanoparticle catalysts with fixed Ce/Ti molar ratio of 0.3 and fixed Cd loading amounts of  $M\%$  were prepared by an improved incipient-wetness impregnation method. In a typical synthesis, the support of 5 g  $\text{Ce}_{0.3}\text{TiO}_x$  was preheated in a vacuum oven at 100 °C to remove the adsorbed water. Then an aqueous solution of  $\text{Cd}(\text{CH}_3\text{COO})_2$  was slowly added to the support at stirring with a glass rod under room temperature, and then ultrasonic treatment for 1 h. The precursor was dried at 100 °C for 12 h, and consequently calcined in air at 500 °C for 6 h. The final catalyst is labeled as  $\text{Cd}_M/\text{Ce}_{0.3}\text{TiO}_x$  ( $M = 1, 2, 3, 5$ , wt%).

## 2.2 Catalyst characterization

Powder XRD patterns were obtained by a powder X-ray diffractometer (Shimadzu XRD 6000) using  $\text{Cu K}\alpha$  ( $\lambda = 0.15406$  nm) radiation with a Nickel filter and operating at 40 kV and 10 mA in the  $2\theta$  range of 5–70° at a scanning rate of  $1^\circ\text{min}^{-1}$ .

$\text{N}_2$  adsorption–desorption isotherm was measured at 77 K using a Micromeritics TriStar II 2020 porosimetry analyzer. The samples were degassed at 300 °C for 8 h prior to the measurements. The specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method.

The surface morphology of the catalyst was observed by field emission scanning electron microscopy (FESEM) on a Quanta 200F instrument using accelerating voltages of 5 kV, in combination with an EDAX genesis 4000 energy-dispersive X-ray spectrometer (EDX). TEM images were carried out using a JEOL JEM 2100 electron microscope equipped with a field emission source at an accelerating voltage of 200 kV.

Temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) measurement was performed on a conventional flow apparatus. Prior to measurements, 100 mg of the sample was pretreated in  $\text{N}_2$  gas ( $60\text{ cm}^3\text{ min}^{-1}$ ) at 500 °C for 0.5 h and then cooled down to room temperature. Next, the sample was exposed to a mixed gas (10 vol%  $\text{NH}_3$  and 90 vol%  $\text{N}_2$ ) flow of  $30\text{ cm}^3\text{ min}^{-1}$  for 0.5 h to ensure the sufficient adsorption of  $\text{NH}_3$ . Before desorption, the sample was flushed in  $\text{N}_2$  gas for 1.5 h. Subsequently,  $\text{NH}_3$  desorption was performed in the range of 50–600 °C at a heating rate of  $10^\circ\text{C min}^{-1}$  under a  $\text{N}_2$  flow of  $30\text{ cm}^3\text{ min}^{-1}$ .

*In situ* DRIFTS were recorded using a thermo Nicolet IS50 spectrometer, which was equipped with a high temperature environmental cell fitted with Zn–Se 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  $50\text{ cm}^3\text{ min}^{-1}$  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 *in situ* DRIFTS spectra were recorded by accumulating 64 scans with a resolution of  $4\text{ cm}^{-1}$ .

## 2.3 Catalytic activity measurement

$\text{NH}_3$ -SCR activity measurements were carried out in a fixed bed quartz micro-reactor operating in a steady flow mode. 0.4 g of

catalysts were sieved with 40–60 mesh and used in each test. The reactant gas included 1000 ppm NO, 1000 ppm  $\text{NH}_3$ , 3%  $\text{O}_2$  and balance  $\text{N}_2$ . The total flow rate was  $500\text{ cm}^3\text{ min}^{-1}$  and thus a GHSV of  $45\,000\text{ h}^{-1}$  was obtained. The temperature varied from 100 to 500 °C, and heating rate was  $3^\circ\text{C min}^{-1}$ . The data was recorded when the temperature hold at each point for more than 5 min. The concentration of  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) in the inlet and outlet gas mixture was measured by a SIGNAL 4000 VM  $\text{NO}_x$  analyzer. Meanwhile, the concentration of  $\text{NH}_3$ , NO,  $\text{NO}_2$  and  $\text{N}_2\text{O}$  were measured by a FTIR spectrometer (MKS, Multi Gas 2030HS).

NO conversion and  $\text{N}_2$  selectivity are calculated in the following eqn (1) and (2).

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

$$\text{N}_2 \text{ selectivity} =$$

$$\left( 1 - \frac{2[\text{N}_2\text{O}]_{\text{outlet}}}{[\text{NO}_x]_{\text{inlet}} + [\text{NH}_3]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}} - [\text{NH}_3]_{\text{outlet}}} \right) \times 100\% \quad (2)$$

# 3. Results and discussion

## 3.1 XRD results

XRD was employed to analyze the phase structure of all the catalysts. Fig. 1 shows the XRD patterns of  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  mixed-oxide catalysts. Crystalline phases were identified by comparison with ICDD files (anatase  $\text{TiO}_2$ , 21-1272;  $\text{CeO}_2$ , 34-0394). Among them, titanium oxide was a dominating phase. As shown in Fig. 1, the diffraction peaks at 25.58°, 28.62°, 47.61°, 56.47°, are ascribed to the characteristic reflections of anatase  $\text{TiO}_2$ . There is no peak at 27.5° in the samples, which indicates that there is no rutile titania existing in all samples.<sup>17,18</sup> Moreover, there is a characteristic peak assigned to Cd oxide (peak at 33.24°).<sup>19</sup> This indicates that Cd oxides are dispersed over  $\text{Ce}_{0.3}\text{TiO}_x$  support for  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  samples.

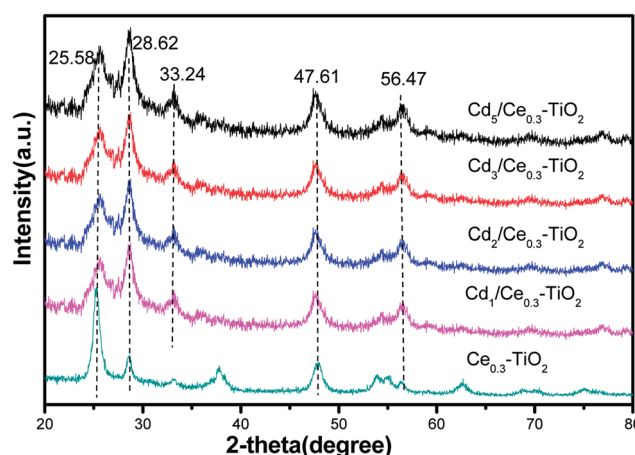
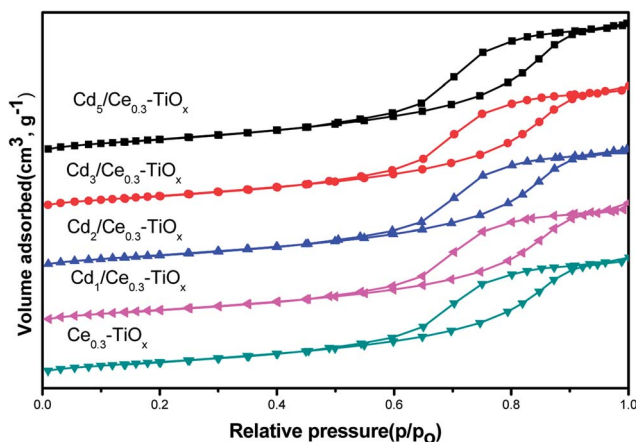


Fig. 1 XRD patterns of the  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts.



**Table 1** BET surface areas and structural parameters of  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts

Sample	$S_{\text{BET}}^a$ ( $\text{m}^2 \text{g}^{-1}$ )	$d_p^b$ (nm)	$V_p^b$ ( $\text{cm}^3 \text{g}^{-1}$ )
$\text{Ce}_{0.3}\text{-TiO}_x$	45.8	7.9	0.15
$\text{Cd}_1/\text{Ce}_{0.3}\text{-TiO}_x$	69.0	7.4	0.18
$\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$	67.1	7.3	0.18
$\text{Cd}_3/\text{Ce}_{0.3}\text{-TiO}_x$	57.7	7.4	0.16
$\text{Cd}_5/\text{Ce}_{0.3}\text{-TiO}_x$	56.9	7.5	0.17

<sup>a</sup> Calculated by BET method. <sup>b</sup> Calculated by *t*-plot method.**Fig. 2** Nitrogen adsorption-desorption isotherms of the  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts.

### 3.2 $\text{N}_2$ adsorption-desorption results

BET surface areas and structural parameters of  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts were measured by  $\text{N}_2$  adsorption-desorption. Table 1 summarizes the surface area ( $S_{\text{BET}}$ ), pore volume ( $V_p$ ), and pore diameter ( $d_p$ ) of different samples, calculated by the BJH method based on the  $\text{N}_2$  adsorption-desorption isotherms. It is clear that  $\text{Ce}_{0.3}\text{-TiO}_x$  exhibits the lowest  $S_{\text{BET}}$  values about  $45.8 \text{ m}^2 \text{g}^{-1}$ , while all  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  exhibit the higher  $S_{\text{BET}}$  values about  $56.9\text{--}69.0 \text{ m}^2 \text{g}^{-1}$ . It may be due to an interaction between  $\text{Ce}_{0.3}\text{-TiO}_x$  and  $\text{CH}_3\text{COO}^-$  ions. In the process of impregnation,  $\text{Cd}(\text{CH}_3\text{COO})_2$  was used. The pore wall of the support  $\text{Ce}_{0.3}\text{-TiO}_x$  was acid corrosion by  $\text{CH}_3\text{COO}^-$  ions and the pore volume of the catalysts was enlarged. Thus,  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  exhibits the higher  $S_{\text{BET}}$  values. BET surface area decreases when Cd contents increase. It may be due to excess Cd blocking the pores of the catalysts with the increasing of Cd contents.  $\text{N}_2$  adsorption-desorption result also shows that all samples contain mesopores with a relatively uniform pore size around 7 nm. Meanwhile, the isotherm curves of  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts show typical H1 hysteresis loop (Fig. 2). It indicates the mesoporous structure of the mixed oxide.<sup>20</sup> The pore size distribution is concentrated. There is no additional pore-forming material was used in the process of catalyst preparation. Thus, the mesoporous structure may be produced by the aggregation of nanoparticles.

### 3.3 SEM results

The microstructure of all catalysts was further investigated by SEM. In Fig. 3a,  $\text{Ce}_{0.3}\text{-TiO}_x$  sample is composed of irregularly localized and distinct edged particles within the regular geometry (nanoparticles). The images in Fig. 3b–e show the agglomeration degree of catalysts varies with different Cd loading amounts. There is no obvious effect on the catalyst morphology when Cd content is low. However, when the loading amount is more than 3 wt%, the catalyst surface agglomeration becomes slightly clear.

### 3.4 TEM results

TEM image of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  nanoparticle catalyst is shown in Fig. 4. The lattice fringe, which is marked as 0.35 nm in the HRTEM image of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$ , belongs to (101) planes of anatase  $\text{TiO}_2$ .<sup>20,21</sup> The lattice fringe, which is marked as 0.32 nm in the HRTEM image of  $\text{Ce}_{0.3}\text{-TiO}_2$ , belongs to (111) planes of  $\text{CeO}_2$ .  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  nanocomposites show a uniform distribution and small particle sizes. The mean diameters were analyzed by statistical analysis of more than 100 particles in TEM images. The average particle size is 20 nm for  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts. The sample displays a uniform distribution of particle sizes.

### 3.5 $\text{NH}_3$ -TPD results

Temperature-programmed desorption of ammonia was carried out to determine the strength and amount of different acid sites.  $\text{NH}_3$ -TPD patterns of  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts are depicted in Fig. 5. All catalysts show two shoulder peaks in the ranged  $140\text{--}360^\circ\text{C}$  and  $450\text{--}600^\circ\text{C}$ , respectively. The ammonia desorbed at low temperatures is ascribed to the weak acidic sites, which is corresponding to the partially ionic  $\text{NH}_4^+$  bound to Brønsted acid sites. And the ammonia desorbed at high temperature was ascribed to the desorption of co-ordinated  $\text{NH}_3$  bound Lewis acid sites.<sup>6,22,23</sup>

Furthermore, the intensity and the area of  $\text{NH}_3$  desorption over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  is higher than the other catalyst. The comparison of the area of the desorbed  $\text{NH}_3$  over  $\text{Ce}_{0.3}\text{-TiO}_x$ ,  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  and  $\text{Cd}_5/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts is 1 : 1.06 : 0.87. The ammonia adsorption ability of the catalyst is generally considered as one of the most important criteria for the screening of catalytic systems for the  $\text{NH}_3$ -SCR.<sup>6,22,23</sup> As was shown in Fig. 5,  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst showed more desorbed ammonia at low temperature. It seems that the proper content of Cd catalyst possesses more weak acidic sites. Thus, the improvement in ammonia adsorption over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst is believed to be significantly beneficial to the  $\text{NO}_x$  reduction by ammonia.

### 3.6 $\text{NH}_3$ -SCR activities

Fig. 6 shows the results of NO conversion in  $\text{NH}_3$ -SCR reaction over  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts in the temperature range of  $175\text{--}400^\circ\text{C}$ , and Fig. 7 shows the  $\text{N}_2$  selectivity of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts in the temperature range of  $175\text{--}400^\circ\text{C}$ . And a commercial  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$  catalyst was used as a ref. 6, 24 and 25. When appropriate amounts of Cd are loaded to  $\text{Ce}_{0.3}\text{-}$





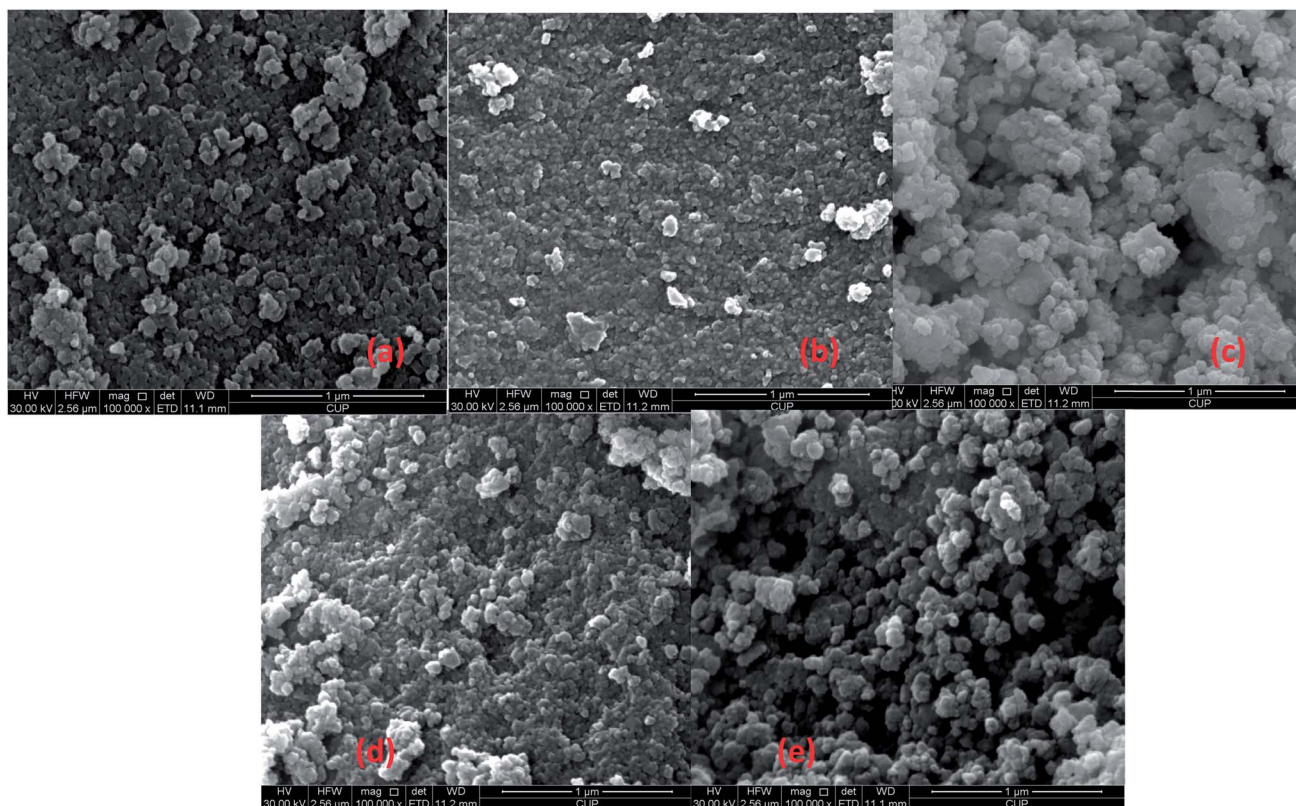


Fig. 3 SEM images of different catalysts: (a)  $\text{Ce}_{0.3}\text{-TiO}_x$ , (b)  $\text{Cd}_1/\text{Ce}_{0.3}\text{-TiO}_x$  (c)  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  (d)  $\text{Cd}_3/\text{Ce}_{0.3}\text{-TiO}_x$  (e)  $\text{Cd}_5/\text{Ce}_{0.3}\text{-TiO}_x$ .

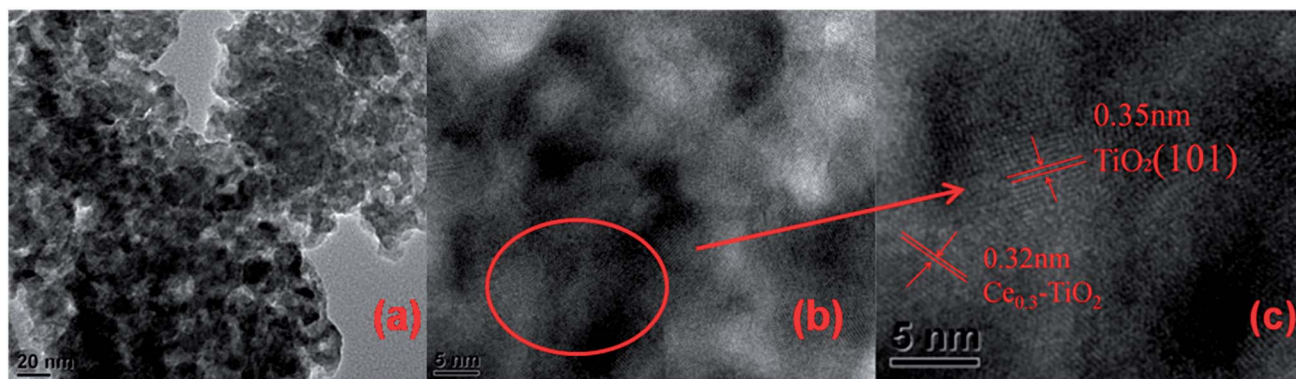


Fig. 4 TEM images of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts.

$\text{TiO}_x$ , a significant influence on catalytic activity is observed. The temperature range for optimum NO reduction (>90%) extends toward wider temperature window. Among all the catalysts tested in this study,  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst exhibits the widest temperature window of catalytic activity for the removal of NO. The highest temperature to maintain NO conversion of 90% is 400 °C. For  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst, the temperature range is between 250 °C and 400 °C for NO removal above 90%. Meanwhile, the large amounts of Cd addition (3 wt% and 5 wt%) lead to a decreasing activity, which may be due to the occurrence of unselective oxidation of  $\text{NH}_3$ . The catalytic performances of  $\text{Cd}_1/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst and  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst are very

similar in the temperature range between 325 and 400 °C. However, the catalytic behaviours of  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts are associated with the amount of Cd addition in the whole temperature range.

$\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  exhibits the highest catalytic activity among  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts. In the temperature range of 250–400 °C,  $\text{NO}_x$  conversion exceeds 90%, which is better than the commercial V–W–Ti catalyst. More remarkably,  $\text{N}_2$  selectivity is kept above 96% in the range of 175–400 °C, while the  $\text{N}_2$  selectivity of V–W–Ti catalyst is 87% at 400 °C.

Cd belongs to IIB elements and its main valence state is  $\text{Cd}^{2+}$ . Similar to  $\text{TiO}_2$ , Cd has also exhibited very high photocatalytic



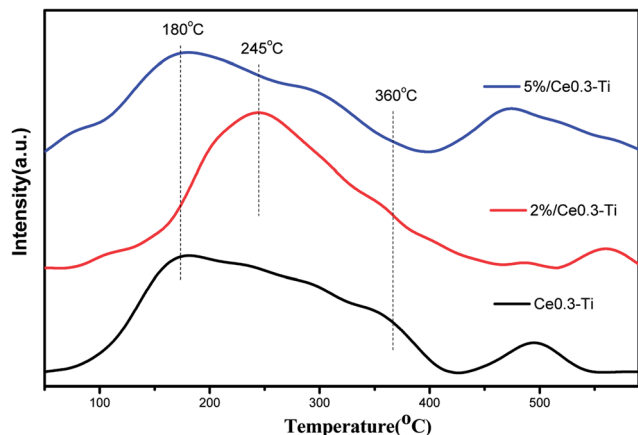


Fig. 5  $\text{NH}_3$ -TPD curves of  $\text{Ce}_{0.3}\text{-TiO}_x$ ,  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  and  $\text{Cd}_5/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts.

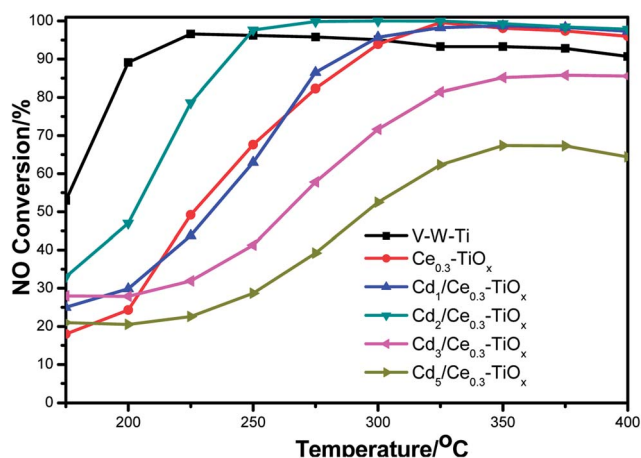


Fig. 6 NO conversion as a function of reaction temperature over  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalysts.

activity.<sup>15,16</sup> It may indicate that there is the strong interaction a synergistic effect between Cd and  $\text{TiO}_x$ . And a proper content of Cd promotes the catalytic activity of  $\text{Cd}_M/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst for

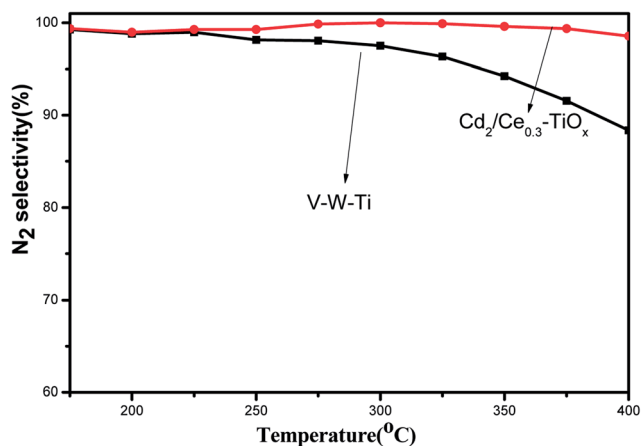


Fig. 7  $\text{N}_2$  selectivity as a function of reaction temperature over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  and V-W-Ti catalysts.

$\text{NH}_3$ -SCR reaction. The NO conversion in  $\text{NH}_3$ -SCR reaction show that 2 wt%  $\text{Cd}/\text{Ce}_{0.3}\text{-TiO}_x$  is the better than other samples. It may be due to more uniformly catalyst particles, bigger surface area and excellent physicochemical properties.

Furthermore, it should be noted that the NO conversion decreased at 400 °C or higher temperature and the NO conversion decreases with the increasing of the reaction temperature due to the more unselective oxidation of  $\text{NH}_3$ .

### 3.7 In situ DRIFTS results over $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$ catalyst

(1) **Adsorption of  $\text{NH}_3$ .** The *in situ* DRIFTS of  $\text{NH}_3$  adsorption over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst at different temperatures is shown in Fig. 8. When  $\text{NH}_3$  gas is introduced into the DRIFTS cell at room temperature, several vibration bands can be detected in the range of 1000–4000  $\text{cm}^{-1}$ . The bands at 1163 and 1207  $\text{cm}^{-1}$  can be assigned to the asymmetric and symmetric bending vibrations of N–H bond in  $\text{NH}_3$  coordinately linked to Lewis acid site, respectively. The bands at 3354, 3258 and 3153  $\text{cm}^{-1}$  can be ascribed to the N–H stretching vibration modes of the coordinated  $\text{NH}_3$ , while the band at 1435  $\text{cm}^{-1}$  with a shoulder at 1472  $\text{cm}^{-1}$  is ascribed to the asymmetric bending vibration of NH bond in  $\text{NH}_4^+$  chemisorbed on Brønsted acid site.<sup>26,27</sup> These Lewis acid sites on the surface of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst decrease slowly with the increasing of the reaction temperature. However, it is noticeable that the bands at 1435 and 1472  $\text{cm}^{-1}$  are disappeared above 150 °C. It means that those Brønsted acid sites are weak acid sites. The obtained results suggested that at a temperature lower than 200 °C these adsorbed  $\text{NH}_3$  species are stable. With the increasing of the temperature,  $\text{NH}_3$  is easy to desorb from the weak Brønsted acid sites on the surface of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst. However, it is stable adsorption on the Lewis acid sites. It has been reported that Brønsted acid site is beneficial for the adsorption of  $\text{NH}_3$ , thus improving the low-temperature activity.

(2) **Co-adsorption of NO and  $\text{O}_2$ .** Fig. 9 shows the *in situ* DRIFTS spectra of NO +  $\text{O}_2$  desorption on  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst at different temperatures. Several distinct bands appeared at

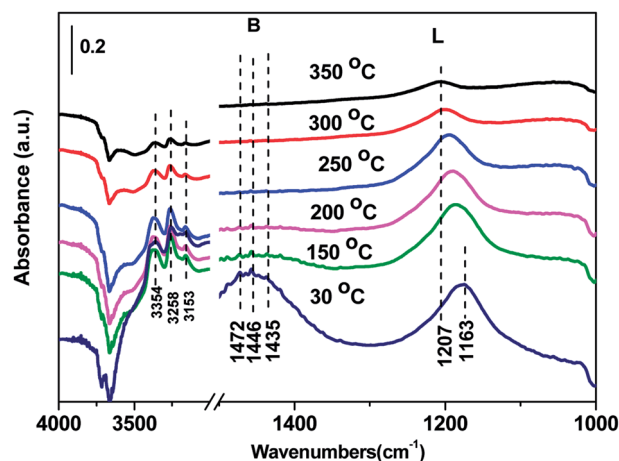


Fig. 8 *In situ* DRIFTS of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  treated in flowing 500 ppm  $\text{NH}_3$  at room temperature for 60 min and then purged by  $\text{N}_2$  at 30, 150, 200, 250, 300, 350 °C.





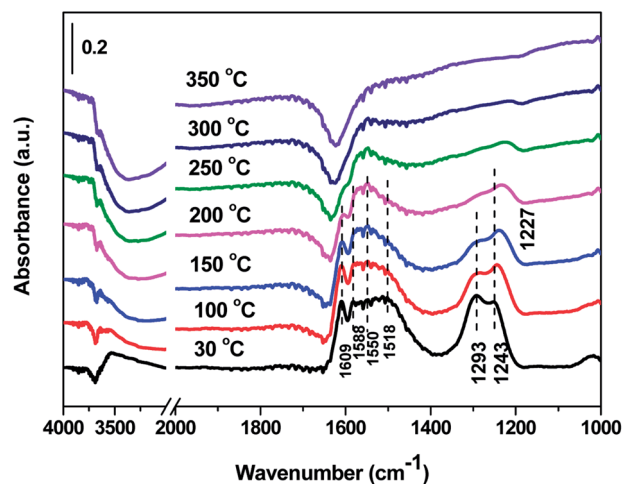


Fig. 9 *In situ* DRIFTS of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  treated in flowing 500 ppm  $\text{NO} + 3\% \text{O}_2$  at room temperature for 60 min and then purged by  $\text{N}_2$  at 30, 100, 150, 200, 250, 300, 350 °C.

1243, 1293, 1518, 1588 and 1609  $\text{cm}^{-1}$  at room temperature, which was respectively assigned to the asymmetric frequency of gaseous  $\text{NO}_2$  molecules (1609  $\text{cm}^{-1}$ ), bidentate nitrate (1588  $\text{cm}^{-1}$ ), monodentate nitrate (1293 and 1518  $\text{cm}^{-1}$ ), bridged nitrate (1243  $\text{cm}^{-1}$ ). At the temperature 100 °C, the bands ascribed to monodentate nitrate vanished, while the peaks attributed bridged bidentate nitrite (1227  $\text{cm}^{-1}$ ) and chelating bidentate nitrate (1550  $\text{cm}^{-1}$ ) appeared, suggesting a redox conversion from monodentate nitrate and bidentate nitrate to *cis*- $\text{N}_2\text{O}_2^{2-}$ , bridged bidentate nitrite and monodentate nitrite over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst.<sup>28–30</sup> With the increasing of the temperature, all bands attributed to  $\text{NO}_x$  species vanish gradually, indicating that the absorbed nitrate and nitrite species were decomposed or inhibited.

(3) **Reaction between nitrogen oxides and ammonia adspecies.** Fig. 10 shows the *in situ* DRIFTS spectra of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst as a function of time in a flow of  $\text{NO} + 3\% \text{O}_2$  after

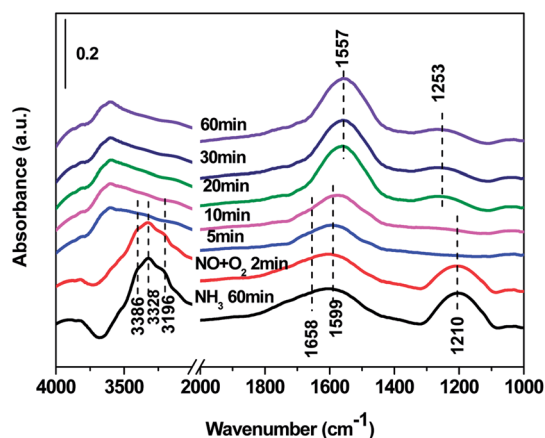


Fig. 10 *In situ* DRIFTS over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst as a function of time in a flow of  $\text{NO} + 3\% \text{O}_2$  after the catalysts was pre-exposed to a flow of  $\text{NH}_3$  for the 60 min followed by  $\text{N}_2$  purging for 30 min at 250 °C.

the catalysts is pre-exposed to a flow of  $\text{NH}_3$  for the 60 min followed by  $\text{N}_2$  purging for 30 min at 250 °C. The coordinated  $\text{NH}_3$  on Lewis acid sites (1210 and 1599  $\text{cm}^{-1}$ ) and Brønsted acid site (1658  $\text{cm}^{-1}$ ) were formed after feeding  $\text{NH}_3$ . The bands at 3386, 3328 and 3196  $\text{cm}^{-1}$  can be ascribed to the N–H stretching vibration modes of the coordinated  $\text{NH}_3$ . All the band due to ammonia adspecies diminish in 10 min after  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst is purged by  $\text{NO} + \text{O}_2$ , and subsequently the absorbed  $\text{NO}_2$  (1253 and 1557  $\text{cm}^{-1}$ ) is observed. It was noticeable that the bands assigned to  $\text{NO}_x$  species (1606 and 1579  $\text{cm}^{-1}$ ) are absent and only two bands related to  $\text{NO}_2$  appear, indicating that the adsorption of nitrate species is inhibited.<sup>26–32</sup>

(4) **Reaction between ammonia and adsorbed nitrogen oxides species.** Fig. 11 shows the *in situ* DRIFTS spectra of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst as a function of time in a flow of  $\text{NH}_3$  after the catalyst is pre-exposed to a flow of  $\text{NO} + 3\% \text{O}_2$  for the 60 min followed by  $\text{N}_2$  purging for 30 min at 250 °C. The band for the absorbed  $\text{NO}_2$  (1610  $\text{cm}^{-1}$ ) vanished in 5 min after  $\text{NH}_3$  were introduced into the system. Simultaneously, the peaks ascribed to coordinated  $\text{NH}_3$  on Lewis acid sites (3373, 3259, 3162, 1599 and 1205  $\text{cm}^{-1}$ ) and  $\text{NH}_4^+$  species on Brønsted acid sites (1429 and 1662  $\text{cm}^{-1}$ ) appear.

(5) ***In situ* DRIFTS spectra in a flow of  $\text{NO} + \text{NH}_3 + \text{O}_2$ .** Fig. 12 shows the *in situ* DRIFTS spectra of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst in a flowing of 1000 ppm  $\text{NH}_3 + 1000$  ppm  $\text{NO} + 3\% \text{O}_2$  at various temperatures under the steady-state condition.  $\text{NO}$  band assigned to  $\text{NO}_x$  species is detected in the whole region, which results in the competitive adsorption and follows the reactions among  $\text{NH}_3$ . With the temperature increasing, the intensity of the bands assigned to  $\text{NH}_4^+$  species on Brønsted acid sites (1442, 1674  $\text{cm}^{-1}$ ) decrease faster than that of the bands ascribed to coordinated  $\text{NH}_3$  on Lewis acid sites (3363, 3264, 3168 and 1596  $\text{cm}^{-1}$ ).<sup>26–32</sup> The adsorbed  $\text{NH}_3$  species on Brønsted acid site disappeared completely at 200 °C, while the band at 1203  $\text{cm}^{-1}$  attributed to the symmetric bending vibrations of N–H bond in  $\text{NH}_3$  coordinately linked to Lewis acid site is also detected even at 350 °C.

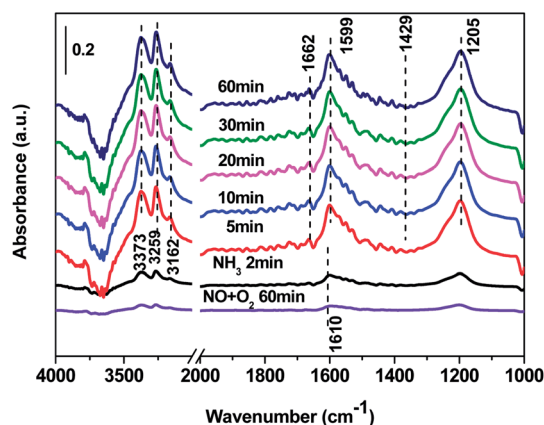


Fig. 11 *In situ* DRIFTS over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst as a function of time in a flow of  $\text{NH}_3$  after the catalysts was pre-exposed to a flow of  $\text{NO} + 3\% \text{O}_2$  for the 60 min followed by  $\text{N}_2$  purging for 30 min at 250 °C.



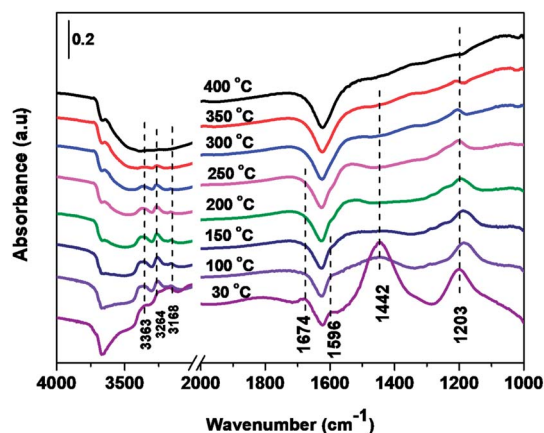


Fig. 12 *In situ* DRIFTS spectra of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst in a flowing of 1000 ppm  $\text{NH}_3$  + 1000 ppm  $\text{NO}$  + 3%  $\text{O}_2$  at 30, 100, 150, 200, 250, 300, 350 and 400 °C.

*In situ* DRIFTS spectra over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst show that there is the adsorbed  $\text{NH}_3$  species on both Lewis and Brønsted acid site, and the adsorbed nitrate and nitrite species form on the surface of catalyst at room temperature. While when the temperature exceeds 150 °C, all bands attributed to  $\text{NO}_x$  and  $\text{NH}_3$  species vanish gradually except the bands attributed to adsorbed  $\text{NH}_3$  species on Lewis acid site.

(6) **L-H mechanism and E-R-oriented mechanism.** The *in situ* DRIFTS spectra indicate that the reaction between adsorbed  $\text{NO}_2$  and  $\text{NH}_3$  easily occurred over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst. Combining with the result of  $\text{NO}$  + 3%  $\text{O}_2$  adsorption *in situ* DRIFTS, the adsorption of nitrate species is significantly limited, leading to more active sites available for the adsorption and activation of  $\text{NH}_3$  thus exhibiting a higher activity. *In situ* DRIFTS spectra in a flow of  $\text{NO}$  +  $\text{NH}_3$  +  $\text{O}_2$  exhibits that all the adsorbed  $\text{NH}_3$  species on Lewis acid site is detected even at 350 °C. However,  $\text{NH}_3$  is easy to desorb from the weak Brønsted acid site at 200 °C. Thus, this phenomenon may be due to the adsorbed  $\text{NH}_3$  species on Lewis acid site are very stable and react with  $\text{NO}_2$  or  $\text{NO}$  from the gas phase at 350 °C.

On the one hand, ammonia and nitrogen oxides were adsorbed in low temperature,  $\text{NH}$  bond in  $\text{NH}_4^+$  chemisorbed on acid sites and the bands attributed to  $\text{NO}_x$  species are obvious. The reaction between adsorbed  $\text{NO}_x$  and adsorbed ammonia is related to the L-H mechanism. On the other hand, the adsorbed nitrate and nitrite species were decomposed at the high temperature, and the adsorbed ammonia decreased slowly. The reaction between adsorbed ammonia and  $\text{NO}_2$  or  $\text{NO}$  from the gas phase is corresponding to E-R-oriented mechanism. Thus the *in situ* DRIFTS spectra of  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst show that, the main L-H mechanism may gradually transform to E-R-oriented mechanism with the increasing of the temperature.<sup>26–32</sup>

## 4. Conclusion

$\text{Ce}_{0.3}\text{-TiO}_x$  nanoparticle carrier was prepared by the sol-gel method, and a series of Cd-Ce-Ti nanoparticle catalysts with

variable Cd contents were prepared by the means of an improved incipient-wetness impregnation. The loading amount of Cd in the catalysts affects the  $\text{NH}_3\text{-SCR}$  catalytic activity and physicochemical properties. SEM, TEM and  $\text{N}_2$  adsorption-desorption results show that the catalyst particle distributes uniformly and all catalysts contain the mesoporous structure from overlapped nanoparticles.

The  $\text{NH}_3\text{-TPD}$  results indicate that the intensity and the area of  $\text{NH}_3$  desorption over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  is higher than the other catalyst. The improvement in ammonia adsorption over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst is beneficial to the  $\text{NO}_x$  reduction by ammonia. Among all the catalysts,  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst exhibits the widest temperature window for the removal of  $\text{NO}$  and the temperature range is between 250 and 400 °C for  $\text{NO}$  removal above 95%, and the  $\text{N}_2$  selectivity is kept above 96% in the full temperature range.

*In situ* DRIFTS spectra over  $\text{Cd}_2/\text{Ce}_{0.3}\text{-TiO}_x$  catalyst show that when the temperature exceeds 150 °C, the adsorbed  $\text{NH}_3$  species on Lewis acid sites play more important role than those on Brønsted acid sites. With the increasing of the temperature, the main L-H mechanism may gradually transform to E-R-oriented mechanism.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 M. G. Schultz, T. Diehl, G. P. Brasseur and W. Zittel, *Science*, 2003, **302**, 624.
- 2 Q. Liang, Z. Zhao, J. Liu, Y. Wei, G. Jiang and A. Duan, *Acta Phys.-Chim. Sin.*, 2014, **30**, 129.
- 3 A. Tomita, T. Yoshii, S. Teranishi, M. Nagao and T. Hibino, *J. Catal.*, 2007, **247**, 137.
- 4 X. Zhao, L. Huang, H. Li, H. Hu, J. Han, L. Shi and D. Zhang, *Chin. J. Catal.*, 2015, **36**, 1886.
- 5 K. Zhao, W. Han, Z. Tang, G. Zhang, J. Lu, G. Lu and X. Zhen, *Colloids Surf., A*, 2016, **503**, 53.
- 6 K. Cheng, J. Liu, Z. Zhao, Y. Wei, G. Jiang and A. Duan, *RSC Adv.*, 2015, **5**, 45172.
- 7 H. He, F. Liu, Y. Yu and W. Shan, *Sci. China: Chem.*, 2012, **42**, 442.
- 8 P. R. Ettireddy, N. Ettireddy, S. Mamedov, P. Boolchand and P. Smimiotis, *Appl. Catal., B*, 2007, **76**, 123.
- 9 J. Huang, Z. Tong, Y. Huang, Y. Huang and J. Zhang, *Appl. Catal., B*, 2008, **78**, 309.
- 10 S. Bai, W. Lu, D. Li, X. Li, Y. Fang and L. Yuan, *Acta Phys.-Chim. Sin.*, 2014, **30**, 1107.



- 11 Z. Liu, S. Zhang and J. Li, *Appl. Catal., B*, 2014, **158**, 11.
- 12 W. Shan, F. Liu, H. He, C. Deng and X. Zi, *Catal. Commun.*, 2014, **59**, 226.
- 13 C. Xu, J. Liu, Z. Zhao, F. Yu, K. Cheng, Y. Wei, A. Duan and G. Jiang, *J. Environ. Sci.*, 2015, **31**, 74.
- 14 R. Wang, L. Lan, M. Gong and Y. Chen, *Acta Phys.-Chim. Sin.*, 2016, **32**, 1747.
- 15 X. Lu, D. Zheng, J. Gan, Z. Liu, C. Liang, P. Liu and Y. Tong, *J. Mater. Chem.*, 2010, **20**, 9.
- 16 R. Yang, D. Wang, L. Wan and D. Wang, *RSC Adv.*, 2014, **4**, 22162.
- 17 W. Wang, S. Wang, X. Ma and J. Gong, *Catal. Today*, 2009, **148**, 323.
- 18 P. Li, Y. Xin, Q. Li, Z. Wang, Z. Zhang and L. Zheng, *Environ. Sci. Technol.*, 2012, **46**, 9600.
- 19 G. Zhao, Y. Yang and T. Ren, *Acta Pet. Sin.*, 2006, **22**, 308.
- 20 G. Leofanti, M. Padovan, G. Tozzola and B. Venturelli, *Catal. Today*, 1998, **41**, 207.
- 21 H. Wang, S. Cao, F. Zheng, F. Yu, Y. Liu, X. Wei and Z. Wu, *Appl. Surf. Sci.*, 2015, **330**, 245.
- 22 L. Chen, J. Li, M. Ge and R. Zhu, *Catal. Today*, 2010, **153**(3), 77–83.
- 23 K. J. Lee, P. A. Kumar, M. S. Maqbool, K. N. Rao, K. H. Song and H. P. Ha, *Appl. Catal., B*, 2013, **142**, 705.
- 24 A. A. Markeb, L. A. Ordosgoitia, A. Alonso, A. Sánchez and X. Font, *RSC Adv.*, 2016, **6**, 56913.
- 25 C. Tang, H. Zhang and L. Dong, *Catal. Sci. Technol.*, 2015, **6**, 1248.
- 26 Z. Liu, S. Zhang, J. Li and L. Ma, *Appl. Catal., B*, 2014, **144**, 90.
- 27 R. Long and R. Yang, *J. Catal.*, 2000, **190**, 22.
- 28 G. Ramis, L. Yi and G. Busca, *J. Catal.*, 1995, **157**, 523.
- 29 F. Liu, H. He, Y. Ding and C. Zhang, *Appl. Catal., B*, 2009, **93**, 194.
- 30 D. A. Peña, B. S. Uphade and P. G. Smirniotis, *J. Catal.*, 2004, **221**, 421.
- 31 Y. Li, Y. Li, Y. Wan, S. Zhan, Q. Guan and Y. Tian, *RSC Adv.*, 2016, **6**, 54926.
- 32 S. Xiong, Y. Liao, H. Dang, F. Qi and S. Yang, *RSC Adv.*, 2015, **5**, 27785.

