

## PAPER



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## Effect of preparation methods on the activity of $\text{VO}_x/\text{CeO}_2$ catalysts for the selective catalytic reduction of $\text{NO}_x$ with $\text{NH}_3$ †

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The effect of preparation methods on the activity of  $\text{VO}_x/\text{CeO}_2$  catalysts for the selective catalytic reduction of  $\text{NO}_x$  with  $\text{NH}_3$  was fully studied.  $\text{VO}_x/\text{CeO}_2$  prepared by a simple homogeneous precipitation method showed higher  $\text{NH}_3$ -SCR activity and higher  $\text{SO}_2$  and  $\text{H}_2\text{O}$  resistance than catalysts prepared by other methods. Lower  $\text{CeO}_2$  crystallinity on the surface, better dispersion of vanadium species, and higher surface concentration of vanadium species together with more acid sites were all responsible for the higher SCR activity of  $\text{VO}_x/\text{CeO}_2$  prepared by the homogeneous precipitation method. The  $\text{NH}_3$ -SCR reaction over  $\text{VO}_x/\text{CeO}_2$  catalysts mainly followed the Eley-Rideal mechanism, in which gaseous  $\text{NO}$  reacted with adsorbed  $\text{NH}_3$  species to finally form  $\text{N}_2$  and  $\text{H}_2\text{O}$ .

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### 1. Introduction

Nitrogen oxides ( $\text{NO}$  and  $\text{NO}_2$ ), one of the major sources of air pollution, result from automobile exhaust gas and industrial combustion of fossil fuels.<sup>1</sup> They contribute to a variety of environmentally harmful effects such as photochemical smog, acid rain, and haze formation.<sup>2</sup> The selective catalytic reduction of  $\text{NO}_x$  with  $\text{NH}_3$  ( $\text{NH}_3$ -SCR) in the presence of excess oxygen has proved to be the most efficient technology for the removal of nitrogen oxides from stationary and mobile sources.<sup>2,3</sup> Many catalysts have been investigated, and  $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$  has been widely applied as an industrial catalyst for many years due to its high catalytic activity and  $\text{SO}_2$  resistance.<sup>4,5</sup> However, some problems remain for the use of  $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ , such as the narrow operation temperature window of 300–400 °C, low  $\text{N}_2$  selectivity and high conversion of  $\text{SO}_2$  to  $\text{SO}_3$  at high temperatures.<sup>4,6,7</sup> In addition, the high concentration of ash containing  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{As}_2\text{O}_3$ , etc. in the flue gas reduces the performance and longevity of  $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$  catalyst in this temperature range.<sup>8,9</sup> Therefore, a lot of studies have been performed to develop new  $\text{NH}_3$ -SCR catalyst systems or to improve vanadium-based catalysts, especially at low temperatures.<sup>10–15</sup>

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† Electronic supplementary information (ESI) available:  $\text{NO}_x$  conversion over  $\text{VO}_x/\text{CeO}_2$  with different loadings; the  $\text{N}_2$  selectivity in  $\text{NH}_3$ -SCR reaction;  $\text{NH}_3$ -SCR activity after  $\text{SO}_2$  poisoning;  $\text{NH}_3/\text{NO}$  conversion in separate  $\text{NH}_3$  or  $\text{NO}$  oxidation reactions; and the band intensity of nitrate species calculated from DRIFTS of  $\text{VO}_x/\text{CeO}_2$  catalysts. See DOI: 10.1039/c4cy00935e

Vanadium-based catalysts with high loading amounts usually exhibit high  $\text{NH}_3$ -SCR activity and  $\text{SO}_2$  resistance at low temperatures.<sup>16,17</sup> For example,  $\text{V}_2\text{O}_5/\text{AC}$  catalysts were found to exhibit high catalytic activity in the  $\text{NO-NH}_3\text{-O}_2$  reaction at low temperatures.<sup>18–20</sup> Therefore, we chose to investigate and optimize vanadium-based catalysts for practical applications. On the other hand, cerium-based catalysts have also been studied extensively due to their high oxygen storage capacity and excellent redox properties, showing high  $\text{NH}_3$ -SCR activity in the medium or high temperature ranges. In our previous study,  $\text{Ce}/\text{TiO}_2$  catalysts have exhibited highly effective  $\text{NH}_3$ -SCR activity.<sup>21,22</sup> Furthermore,  $\text{V}_2\text{O}_5/\text{CeO}_2$  catalysts have also been attracting much attention for their performance in various catalytic reactions. Gu *et al.*<sup>23</sup> have used  $\text{V}_2\text{O}_5/\text{CeO}_2$  catalysts for the selective oxidation of toluene and found that the loading of  $\text{V}_2\text{O}_5$  and the calcination temperature influenced the surface structures of dispersed vanadium species as well as the surface acidity and redox properties, which have significant effects on the catalytic activity. In the  $\text{NH}_3$ -SCR reaction, a previous study by Li *et al.*<sup>24</sup> showed that  $\text{V}_2\text{O}_5/\text{CeO}_2$  catalysts exhibited high  $\text{NH}_3$ -SCR activity at low temperature, and the  $\text{NO}$  conversion increased significantly with increasing  $\text{V}_2\text{O}_5$  loading. It was reported that the  $\text{V}_{0.75}\text{Ce}$  oxide catalyst exhibited higher  $\text{NH}_3$ -SCR activity than the conventional  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst below 350 °C.<sup>25</sup> Although  $\text{V}/\text{Ce}$  oxide catalysts have shown great catalytic activity, their properties are not well understood and should be investigated in more detail. It is also necessary to decrease the vanadium content due to its toxicity.

In many cases, the activity of catalysts is highly dependent on the preparation method. Therefore, in this study we

systematically investigated VO<sub>x</sub>/CeO<sub>2</sub> catalysts in depth, especially the effects of preparation methods on the catalyst structure and activity in NH<sub>3</sub>-SCR of NO<sub>x</sub>. Even with low loading content of vanadia, the catalysts could still exhibit excellent catalytic performance for the DeNO<sub>x</sub> process. In addition, the VO<sub>x</sub>/CeO<sub>2</sub> catalyst prepared by a simple homogeneous precipitation method (VO<sub>x</sub>/CeO<sub>2</sub>(P)) showed higher NH<sub>3</sub>-SCR activity and better SO<sub>2</sub> resistance than catalysts prepared by other methods, mainly due to lower CeO<sub>2</sub> crystallinity on the surface, better dispersion of vanadium species, and higher surface concentration of vanadium species together with more acid sites.

## 2. Experiments

### 2.1 Catalyst synthesis and activity tests

The 3 wt.% VO<sub>x</sub>/CeO<sub>2</sub> catalysts were prepared by four methods: the homogeneous precipitation method, rotary evaporation impregnation, incipient wetness impregnation and the sol-gel method. All of the materials were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and were analytically pure, except the CeO<sub>2</sub> supports which were prepared by the homogeneous precipitation method, as described below.

**Rotary evaporation impregnation.** VO<sub>x</sub>/CeO<sub>2</sub> was prepared by rotary evaporation impregnation method using CeO<sub>2</sub> and an aqueous solution of NH<sub>4</sub>VO<sub>3</sub> (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was added to facilitate the dissolution of NH<sub>4</sub>VO<sub>3</sub>). After impregnation, the excess water was removed using a rotary evaporator at 60 °C. The sample was first dried at 100 °C overnight followed by calcination at 500 °C in air for 3 h. The catalyst was denoted as VO<sub>x</sub>/CeO<sub>2</sub>(V).

**Homogeneous precipitation method.** Aqueous solutions of Ce(NO<sub>3</sub>)<sub>3</sub> and NH<sub>4</sub>VO<sub>3</sub> were mixed at the required mass ratio (the mass ratio of vanadium oxide was controlled at 3 wt.%). Excess urea in the aqueous solution was then added to the mixed solution. The solution was heated to 90 °C and maintained for 12 h under vigorous stirring. After filtration and washing with deionized water, the resulting precipitate was dried at 100 °C overnight and subsequently calcined at 500 °C for 3 h in air. The VO<sub>x</sub>/CeO<sub>2</sub> sample prepared by the homogeneous precipitation method was denoted as VO<sub>x</sub>/CeO<sub>2</sub>(P).

**Incipient wetness impregnation method.** VO<sub>x</sub> was deposited on CeO<sub>2</sub> by conventional pore volume impregnation with an aqueous solution of NH<sub>4</sub>VO<sub>3</sub> in oxalic acid. After ultrasonic processing for 1 h, the material was dried at 100 °C overnight and calcined at 500 °C for 3 h. The VO<sub>x</sub>/CeO<sub>2</sub> sample prepared by the incipient wetness impregnation method was denoted as VO<sub>x</sub>/CeO<sub>2</sub>(I).

**Sol-gel method.** Ce(NO<sub>3</sub>)<sub>3</sub>, NH<sub>4</sub>VO<sub>3</sub> (at a ratio to yield 3 wt.% vanadium oxide) and excess citric acid were mixed in aqueous solution. The resulting mixture was stirred at room temperature for 1 h. The solution was dried at 120 °C for 12 h, resulting in a porous, foam-like solid. The foam-like precursor was calcined at 500 °C for 3 h in air in a

temperature-programmed muffle furnace. The VO<sub>x</sub>/CeO<sub>2</sub> sample prepared by the sol-gel method was denoted as VO<sub>x</sub>/CeO<sub>2</sub>(S).

Before NH<sub>3</sub>-SCR activity testing, the catalysts were pressed, crushed and sieved to 40–60 mesh. The SCR activity tests were performed in a fixed-bed quartz flow reactor at atmospheric pressure. The reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, 5 vol.% H<sub>2</sub>O (when used), 100 ppm SO<sub>2</sub> (when used), N<sub>2</sub> balance. Under ambient conditions, the total flow rate was 500 ml min<sup>-1</sup> and the gas hourly space velocity (GHSV) was 50 000 h<sup>-1</sup>. The effluent gas including NO, NH<sub>3</sub>, NO<sub>2</sub> and N<sub>2</sub>O was continuously analyzed with an FTIR spectrometer (Nicolet Nexus 670) equipped with a heated, low-volume multiple-path gas cell (2 m). FTIR spectra were collected after the SCR reaction reached a steady state, and the NO<sub>x</sub> conversion and N<sub>2</sub> selectivity were calculated as follows:

$$\text{NO}_x \text{ conversion} = \left( 1 - \frac{[\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}}} \right) \times 100\%$$

$$\text{N}_2 \text{ selectivity} = \frac{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}}} \times 100\%$$

### 2.2 Characterization of catalysts

The surface area and pore characterization of the catalysts were obtained from N<sub>2</sub> adsorption/desorption analysis at -196 °C using a Quantachrome Quadrasorb SI-MP. Prior to N<sub>2</sub> physisorption, the catalysts were degassed at 300 °C for 5 h. Surface areas were determined by the BET equation in the 0.05–0.35 partial pressure range. Pore volumes and average pore diameters were determined by the Barrett-Joyner-Halenda (BJH) method from the desorption branches of the isotherms.

Powder X-ray diffraction measurements of the catalysts were performed using a computerized PANalytical X'Pert Pro diffractometer with Cu Kα (λ = 0.15406 nm) radiation. The data of 2θ from 10 to 80° were collected at 8° min<sup>-1</sup> with a step size of 0.07°.

Visible Raman spectra of the VO<sub>x</sub>/CeO<sub>2</sub> catalysts were collected at room temperature using a Spex 1877 D Triplemate spectrometer with a spectral resolution of 2 cm<sup>-1</sup>. A 532 nm diode-pump solid semiconductor (DPSS) laser was used as the excitation source and the power output was about 40 mW. Before measurements, the catalysts were ground well and mounted on a spinning holder to avoid thermal damage during scanning. Raman signals were collected with conventional 90° geometry and the time for recording each spectrum was 1000 ms. The Raman spectra used in this paper were original and unsmoothed.

The H<sub>2</sub>-TPR experiments were performed with a Micromeritics AutoChem 2920 chemisorption analyzer. The samples (50 mg) were pretreated at 300 °C under a flow of

20 vol.% O<sub>2</sub>/Ar (50 ml min<sup>-1</sup>) for 0.5 h in a quartz reactor and cooled down to room temperature (30 °C) followed by Ar purging for 0.5 h. A 50 ml min<sup>-1</sup> gas flow of 10% H<sub>2</sub> in Ar was then passed over the samples through a cold trap to the detector. The reduction temperature was raised at 10 °C min<sup>-1</sup> from 30 to 1000 °C.

X-ray photoelectron spectroscopy (XPS) spectra of the catalysts were recorded with a scanning X-ray microprobe (AXIS Ultra, Kratos Analytical Ltd.) using Al K $\alpha$  radiation (1486.7 eV). All of the binding energies were calibrated using the C 1s peak (BE = 284.8 eV) as the standard.

### 2.3 NH<sub>3</sub>-TPD studies

NH<sub>3</sub>-TPD experiments were performed using a quadrupole mass spectrometer (HPR-20, Hiden Analytical Ltd.) to record the signal of NH<sub>3</sub> ( $m/z$  = 15 for NH). Prior to TPD experiments, the samples (100 mg) were pretreated at 400 °C under a flow of 20 vol.% O<sub>2</sub>/Ar (50 ml min<sup>-1</sup>) for 0.5 h and cooled down to room temperature (30 °C). The samples were then exposed to a flow of 2500 ppm NH<sub>3</sub>/Ar (50 ml min<sup>-1</sup>) at 30 °C for 1 h, followed by Ar purging for another 1 h. Finally, the temperature was raised to 600 °C under Ar flow at a rate of 10 °C min<sup>-1</sup>.

### 2.4 *In situ* DRIFTS studies

*In situ* DRIFTS experiments were performed using an FTIR spectrometer (Nicolet Nexus 670) equipped with a smart collector and an MCT/A detector cooled by liquid nitrogen. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Prior to each experiment, the sample was pretreated at 400 °C for 0.5 h under a flow of 20 vol.% O<sub>2</sub>/N<sub>2</sub> and then cooled to 200 °C. The background spectra were collected under flowing N<sub>2</sub> and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: 300 ml min<sup>-1</sup> total flow rate, 500 ppm NH<sub>3</sub> or/and 500 ppm NO + 5 vol.% O<sub>2</sub>, and N<sub>2</sub> balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm<sup>-1</sup>.

## 3. Results

### 3.1 Catalytic performance

**3.1.1 SCR activity over VO<sub>x</sub>/CeO<sub>2</sub> catalysts.** The NH<sub>3</sub>-SCR activity over VO<sub>x</sub>/CeO<sub>2</sub> with different loadings is shown in Fig. S1†. 3 wt.% VO<sub>x</sub>/CeO<sub>2</sub> showed much higher catalytic activity than 1%, 0.5%, and 0.1% catalysts, especially at 150–300 °C. Due to the toxicity of vanadium to the human body, a vanadium-based catalyst with very high loading was not preferred. Therefore, we chose the 3% VO<sub>x</sub>/CeO<sub>2</sub> catalyst to investigate rather than catalysts with higher loading.

The NO<sub>x</sub> conversion over VO<sub>x</sub>/CeO<sub>2</sub> catalysts prepared by different methods is shown in Fig. 1. It is obvious that the preparation methods affected the catalytic activity, especially in the relatively low temperature range. VO<sub>x</sub>/CeO<sub>2</sub> prepared by the simple homogeneous precipitation method exhibited

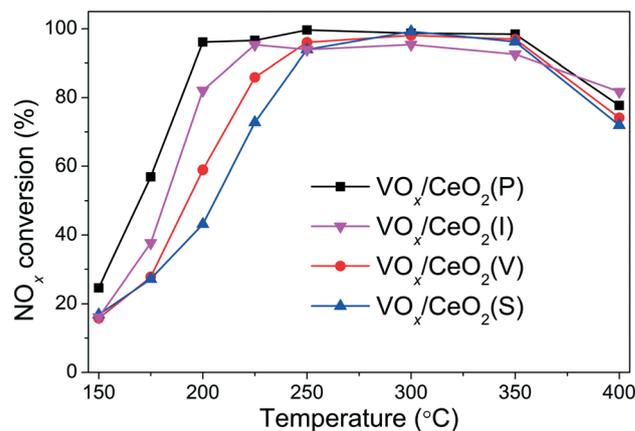


Fig. 1 NH<sub>3</sub>-SCR activity over VO<sub>x</sub>/CeO<sub>2</sub> catalysts prepared by different methods. Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 5 vol.%, N<sub>2</sub> balance, total flow rate 500 ml min<sup>-1</sup> and GHSV = 50 000 h<sup>-1</sup>.

the best catalytic activity, with nearly 100% NO<sub>x</sub> conversion and 100% N<sub>2</sub> selectivity at temperatures above 200 °C. VO<sub>x</sub>/CeO<sub>2</sub> catalysts prepared by rotary evaporation impregnation and incipient wetness impregnation method showed lower NO<sub>x</sub> conversion than that prepared by the homogeneous precipitation method, and the catalyst prepared by the sol-gel method showed the lowest catalytic activity. All of the catalysts presented higher than 90% N<sub>2</sub> selectivity and only a small amount of N<sub>2</sub>O was produced at the temperature that we investigated (as shown in Fig. S2†). The preparation methods could affect the structural properties, redox ability and surface acidity of the catalysts, resulting in different catalytic activities, which will be discussed later in this paper.

**3.1.2 The influence of H<sub>2</sub>O and SO<sub>2</sub> on the SCR activity of VO<sub>x</sub>/CeO<sub>2</sub>.** The NO<sub>x</sub> conversion over VO<sub>x</sub>/CeO<sub>2</sub> catalysts in the NH<sub>3</sub>-SCR reaction with 5 vol.% H<sub>2</sub>O is shown in Fig. 2. Compared to NH<sub>3</sub>-SCR activity without H<sub>2</sub>O, NO<sub>x</sub> conversion

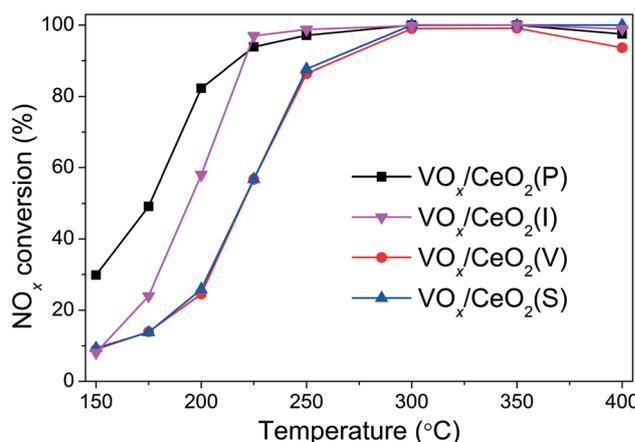


Fig. 2 NO<sub>x</sub> conversion over VO<sub>x</sub>/CeO<sub>2</sub> catalysts in NH<sub>3</sub>-SCR reaction in the presence of H<sub>2</sub>O. Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [H<sub>2</sub>O] = 5 vol.%, [O<sub>2</sub>] = 5 vol.%, N<sub>2</sub> balance, total flow rate 500 ml min<sup>-1</sup> and GHSV = 50 000 h<sup>-1</sup>.

in the presence of H<sub>2</sub>O over the four catalysts at low temperatures decreased in all cases to some degree, while catalytic activity at 400 °C increased from 80% to 100%. The NO<sub>x</sub> conversion over the VO<sub>x</sub>/CeO<sub>2</sub>(P) catalyst at 200 °C was 80%, and only 20% NO<sub>x</sub> conversion was obtained over VO<sub>x</sub>/CeO<sub>2</sub>(S) and VO<sub>x</sub>/CeO<sub>2</sub>(V). The VO<sub>x</sub>/CeO<sub>2</sub>(P) catalyst still exhibited the best catalytic performance in the presence of H<sub>2</sub>O.

Fig. 3 shows the effect of SO<sub>2</sub> on the catalytic activity over VO<sub>x</sub>/CeO<sub>2</sub> catalysts at 250 °C. When 100 ppm SO<sub>2</sub> was introduced to the gas inlet, the NO<sub>x</sub> conversion over VO<sub>x</sub>/CeO<sub>2</sub>(S) decreased rapidly to as low as 60% in 24 h and could not recover to the initial activity after the removal of SO<sub>2</sub>. The NO<sub>x</sub> conversion over VO<sub>x</sub>/CeO<sub>2</sub>(V) and VO<sub>x</sub>/CeO<sub>2</sub>(I) catalysts also decreased, and after the introduction of SO<sub>2</sub>, the catalytic activity recovered to some extent. However, the SO<sub>2</sub> poisoning behaviour over VO<sub>x</sub>/CeO<sub>2</sub>(P) was quite different. The NO<sub>x</sub> conversion decreased slowly, and 93% NO<sub>x</sub> conversion was obtained in the presence of 100 ppm SO<sub>2</sub> for a 24 h test. VO<sub>x</sub>/CeO<sub>2</sub>(P) exhibited the highest catalytic activity and the strongest resistance to SO<sub>2</sub>. The NH<sub>3</sub>-SCR performance of VO<sub>x</sub>/CeO<sub>2</sub> catalysts after SO<sub>2</sub> poisoning for 24 h is shown in Fig. S3.† The activity over VO<sub>x</sub>/CeO<sub>2</sub>(P) was still higher than those over the other catalysts. 100% NO<sub>x</sub> conversion could be obtained over the VO<sub>x</sub>/CeO<sub>2</sub>(P) catalyst at 250 °C and 70% over VO<sub>x</sub>/CeO<sub>2</sub>(S). This proved again that the VO<sub>x</sub>/CeO<sub>2</sub>(P) catalyst showed the strongest SO<sub>2</sub> resistance.

### 3.2 Catalyst characterization

**3.2.1 N<sub>2</sub> physisorption.** The surface areas and pore diameters of VO<sub>x</sub>/CeO<sub>2</sub> catalysts are shown in Table 1. The VO<sub>x</sub>/CeO<sub>2</sub>(P) catalyst exhibited a slightly larger BET surface area and a smaller average pore diameter than VO<sub>x</sub>/CeO<sub>2</sub>(S), which could offer more active sites for reaction and thus be beneficial to NH<sub>3</sub>-SCR activity. The slight difference in the

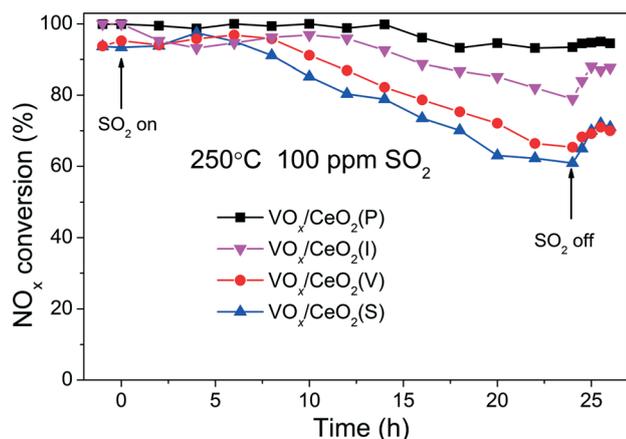


Fig. 3 Effect of SO<sub>2</sub> on the NH<sub>3</sub>-SCR activity over VO<sub>x</sub>/CeO<sub>2</sub> catalysts at 250 °C. Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [SO<sub>2</sub>] = 100 ppm, [O<sub>2</sub>] = 5 vol.%, N<sub>2</sub> balance, total flow rate 500 ml min<sup>-1</sup> and GHSV = 50 000 h<sup>-1</sup>.

Table 1 Surface atomic concentration, BET surface areas and pore diameters of VO<sub>x</sub>/CeO<sub>2</sub> catalysts

Catalysts	Surface atomic concentration <sup>a</sup> (%)			V/Ce atomic ratio	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore diameter (nm)
	Ce	V	O			
VO <sub>x</sub> /CeO <sub>2</sub> (P)	33.5	2.4	64.1	0.072	91.9	5.2
VO <sub>x</sub> /CeO <sub>2</sub> (S)	33.2	1.6	65.2	0.047	88.5	10.5

<sup>a</sup> According to XPS analysis.

specific surface area indicates that the textural structure is not the crucial factor affecting the catalytic performance.

**3.2.2 XRD.** The XRD patterns of VO<sub>x</sub>/CeO<sub>2</sub> catalysts are shown in Fig. 4. For both catalysts, the only crystalline phase observed was CeO<sub>2</sub> (43-1002). No vanadium species such as V<sub>2</sub>O<sub>5</sub> and CeVO<sub>4</sub> were detected, suggesting that V species were highly dispersed on the catalysts. The intensity of the CeO<sub>2</sub> diffraction peaks of the VO<sub>x</sub>/CeO<sub>2</sub>(P) catalyst was stronger than that of VO<sub>x</sub>/CeO<sub>2</sub>(S), indicating that the crystallinity of the CeO<sub>2</sub> phase of VO<sub>x</sub>/CeO<sub>2</sub>(P) was higher than that of VO<sub>x</sub>/CeO<sub>2</sub>(S).

**3.2.3 Raman and XPS.** The surface-sensitive techniques Raman and XPS were employed for characterization of the VO<sub>x</sub>/CeO<sub>2</sub> catalysts. Fig. 5 shows the Raman results for VO<sub>x</sub>/CeO<sub>2</sub>(P) and VO<sub>x</sub>/CeO<sub>2</sub>(S) catalysts. In accordance with previous studies,<sup>22,26</sup> the Raman shift at 453 cm<sup>-1</sup> was attributed to CeO<sub>2</sub> (F<sub>2g</sub> mode). No evidence of vanadium-containing phases, such as V<sub>2</sub>O<sub>5</sub> and CeVO<sub>4</sub>, was detected for either catalyst. The CeO<sub>2</sub> peak intensity for the VO<sub>x</sub>/CeO<sub>2</sub>(P) catalyst was weaker than that for VO<sub>x</sub>/CeO<sub>2</sub>(S), indicating that the CeO<sub>2</sub> crystallinity on the surface of the VO<sub>x</sub>/CeO<sub>2</sub>(P) catalyst was weaker. Active sites could thus be better dispersed on the surface of VO<sub>x</sub>/CeO<sub>2</sub>(P).

Table 1 also shows the surface atomic concentrations of VO<sub>x</sub>/CeO<sub>2</sub> catalysts derived from XPS results. VO<sub>x</sub>/CeO<sub>2</sub>(P) and VO<sub>x</sub>/CeO<sub>2</sub>(S) catalysts exhibited similar surface Ce and O concentrations. The surface V concentration of the VO<sub>x</sub>/CeO<sub>2</sub>(P) catalyst was 2.4%, which is much higher than that of

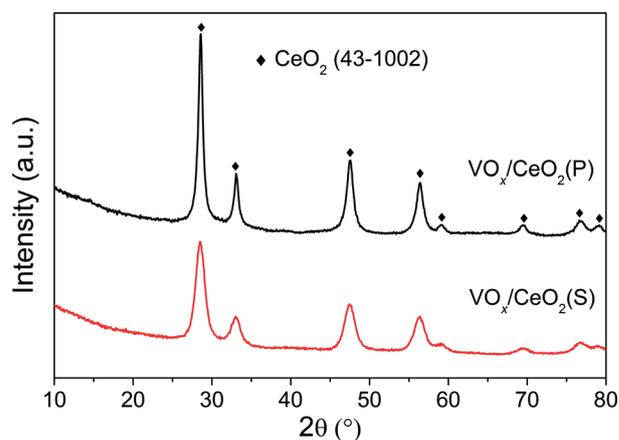


Fig. 4 XRD patterns of VO<sub>x</sub>/CeO<sub>2</sub> catalysts.

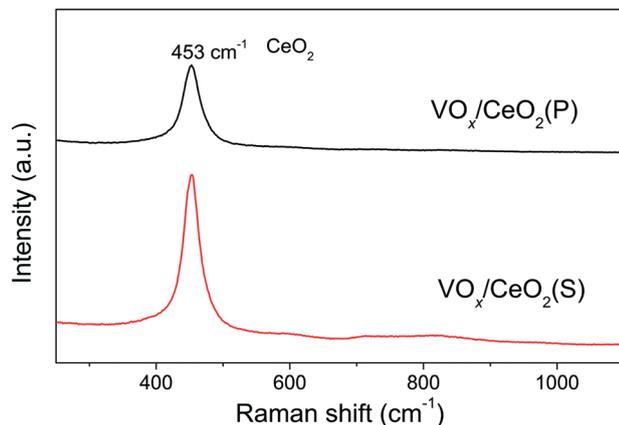


Fig. 5 Raman results of  $\text{VO}_x/\text{CeO}_2$  catalysts.

$\text{VO}_x/\text{CeO}_2(\text{S})$  (1.6%). The V/Ce atomic ratio was 0.072 and 0.047 for  $\text{VO}_x/\text{CeO}_2(\text{P})$  and  $\text{VO}_x/\text{CeO}_2(\text{S})$ , respectively. The higher surface concentration of vanadium species could result in better SCR activity.

**3.2.4  $\text{H}_2$ -TPR.**  $\text{H}_2$ -TPR is frequently used to investigate the redox properties of metal oxide catalysts. Fig. 6 presents the TPR results of  $\text{VO}_x/\text{CeO}_2(\text{P})$  and  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalysts. According to the literature,<sup>27,28</sup> the TPR peak around 480 °C could be attributed to the reduction of surface  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ . The reduction peak of well-dispersed  $\text{V}^{5+}$  species could occur at 460 °C.<sup>29,30</sup> The reduction peak of the  $\text{CeO}_2$  catalyst at 471 °C could be ascribed to the reduction of surface  $\text{Ce}^{4+}$  and the peak at 760 °C could be attributed to the reduction of bulk  $\text{CeO}_2$ . Over the  $\text{VO}_x/\text{CeO}_2(\text{P})$  and  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalysts, the reduction peaks at low temperature showed a much higher intensity than those of the  $\text{CeO}_2$  sample mainly due to the interaction between vanadium and cerium oxides. The  $\text{H}_2$  reduction temperature of the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst was lower than that of  $\text{VO}_x/\text{CeO}_2(\text{S})$  in the low temperature region, and the amount of  $\text{H}_2$  consumption of the former was larger than that of the latter. In addition,  $\text{NO}/\text{NH}_3$  oxidation activity over  $\text{VO}_x/\text{CeO}_2(\text{P})$  was higher than that

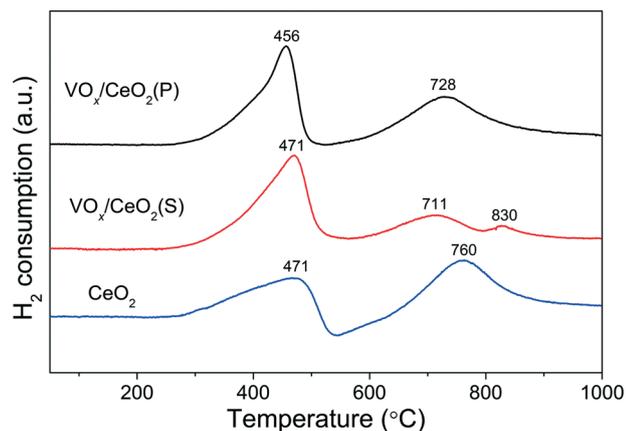


Fig. 6  $\text{H}_2$ -TPR results over  $\text{VO}_x/\text{CeO}_2$  catalysts.

over  $\text{VO}_x/\text{CeO}_2(\text{S})$  (as shown in Fig. S4†). This indicates that the redox capability of the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst was a little greater than that of  $\text{VO}_x/\text{CeO}_2(\text{S})$ , which could contribute to the  $\text{NH}_3$ -SCR activity to some degree.

### 3.3 $\text{NH}_3$ -TPD

Fig. 7 shows  $\text{NH}_3$ -TPD results over  $\text{VO}_x/\text{CeO}_2$  catalysts using the fragment of  $m/z = 15$  ( $\text{NH}$ ) to identify  $\text{NH}_3$ . There were three  $\text{NH}_3$  desorption peaks around 90, 250 and 470 °C on both catalysts. The desorption peaks at 90 °C were ascribed to the desorption of physisorbed  $\text{NH}_3$ . The broad desorption peaks between 150 °C and 400 °C were assigned to weak and moderate acid sites on the catalyst surface. With increasing temperature, small peaks between 400 °C and 600 °C occurred in the  $\text{NH}_3$ -TPD profiles, which are related to  $\text{NH}_3$  molecules adsorbed on the strong acid sites of the catalysts.<sup>31</sup> Although the desorption temperature of  $\text{VO}_x/\text{CeO}_2(\text{P})$  was a little higher than that of the  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalyst, the amount of  $\text{NH}_3$  desorption from the former was notably larger than that from the latter. This indicates that there are more acid sites on the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst.

### 3.4 *In situ* DRIFTS

**3.4.1  $\text{NH}_3$  adsorption.** The *in situ* DRIFT spectra of  $\text{NH}_3$  adsorption on  $\text{VO}_x/\text{CeO}_2(\text{P})$  and  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalysts at 200 °C are shown in Fig. 8(A). After  $\text{NH}_3$  adsorption and  $\text{N}_2$  purging, both catalysts were covered with various  $\text{NH}_3$  species. The bands at 1425  $\text{cm}^{-1}$  were assigned to ionic  $\text{NH}_4^+$  bound to the Brønsted acid sites and the bands at 1594 and 1158  $\text{cm}^{-1}$  were attributed to coordinated  $\text{NH}_3$  bound to the Lewis acid sites.<sup>32,33</sup> The bands at 1260  $\text{cm}^{-1}$  were assigned to the amide species ( $-\text{NH}_2$ ).<sup>33</sup> The  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst exhibited more acid sites than  $\text{VO}_x/\text{CeO}_2(\text{S})$ , including Brønsted acid sites and Lewis acid sites, which was in good agreement with the  $\text{NH}_3$ -TPD results.

**3.4.2  $\text{NO}_x$  adsorption.** Fig. 8(B) shows the DRIFT spectra of  $\text{NO} + \text{O}_2$  adsorption on  $\text{VO}_x/\text{CeO}_2(\text{P})$  and  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalysts at 200 °C. When the  $\text{VO}_x/\text{CeO}_2$  catalyst was exposed

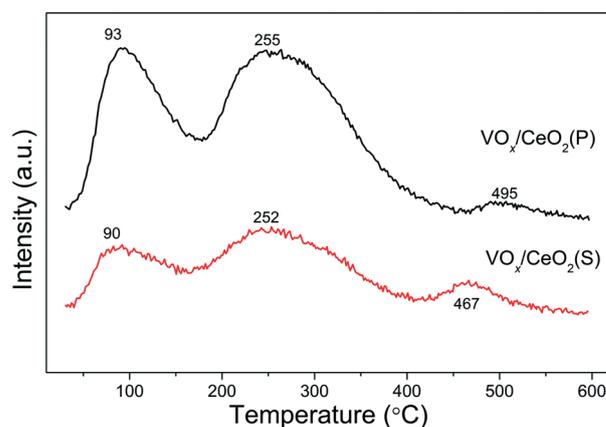


Fig. 7  $\text{NH}_3$ -TPD results of  $\text{VO}_x/\text{CeO}_2$  catalysts.

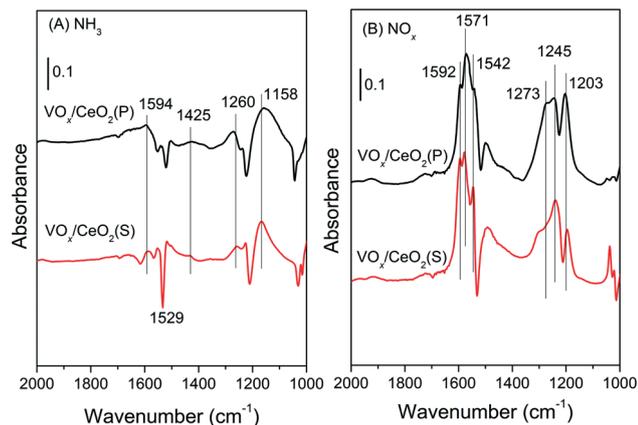


Fig. 8 DRIFT spectra of 500 ppm  $\text{NH}_3$  adsorption (A) and 500 ppm  $\text{NO} + 5 \text{ vol.}\% \text{ O}_2$  adsorption (B) on  $\text{VO}_x/\text{CeO}_2(\text{P})$  and  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalysts.

to  $\text{NO} + \text{O}_2$ , several bands assigned to nitrate species were observed. The bands at 1203 and  $1592 \text{ cm}^{-1}$  could be assigned to bridging nitrate.<sup>34,35</sup> The bands at 1571 and  $1245 \text{ cm}^{-1}$  were ascribed to bidentate nitrate,<sup>32,35,36</sup> while the bands at 1502–1542 and  $1273 \text{ cm}^{-1}$  were attributed to monodentate nitrate.<sup>32,34</sup> The adsorption amount of  $\text{NO}_x$  was larger on the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst than that on  $\text{VO}_x/\text{CeO}_2(\text{S})$ , especially the amount of monodentate nitrate at  $1273 \text{ cm}^{-1}$ .

**3.4.3 In situ DRIFTS of the reaction between  $\text{NO} + \text{O}_2$  species and pre-adsorbed  $\text{NH}_3$  species.** Fig. 9(A) shows the *in situ* DRIFT spectra of the reaction between  $\text{NO} + \text{O}_2$  species and pre-adsorbed  $\text{NH}_3$  species on  $\text{VO}_x/\text{CeO}_2(\text{P})$ . After  $\text{NH}_3$  pre-adsorption and  $\text{N}_2$  purging, the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst surface was covered with various  $\text{NH}_3$  species. When  $\text{NO} + \text{O}_2$  was introduced, the intensity of the bands attributed to  $\text{NH}_3$  species decreased quickly and disappeared after 5 min. At the same time, bands assigned to nitrate species (monodentate nitrate at 1542,  $1273 \text{ cm}^{-1}$ , bridging nitrate at 1203,  $1597 \text{ cm}^{-1}$  and bidentate nitrate at 1571,  $1245 \text{ cm}^{-1}$ ) appeared.

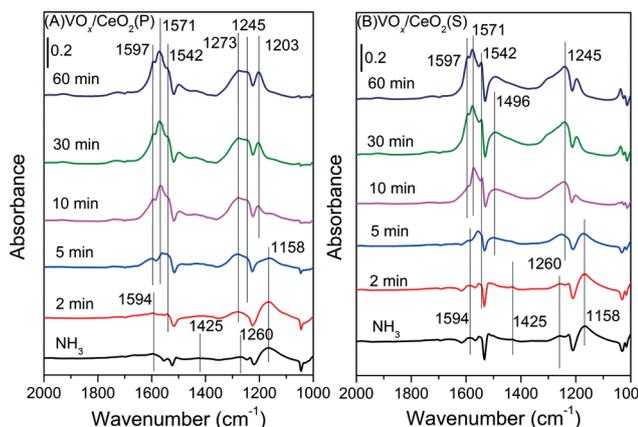


Fig. 9 *In situ* DRIFT spectra of  $\text{VO}_x/\text{CeO}_2(\text{P})$  (A) and  $\text{VO}_x/\text{CeO}_2(\text{S})$  (B) pretreated by exposure to 500 ppm  $\text{NH}_3$  followed by exposure to 500 ppm  $\text{NO} + 5 \text{ vol.}\% \text{ O}_2$  at  $200 \text{ }^\circ\text{C}$ .

This result suggested that the adsorbed  $\text{NH}_3$  species, including ionic  $\text{NH}_4^+$  and coordinated  $\text{NH}_3$ , could both react with  $\text{NO}_x$  and participate in the  $\text{NH}_3$ -SCR reactions.

For the  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalyst (Fig. 9(B)), similar bands due to  $\text{NH}_3$  adsorption were observed after  $\text{NH}_3$  pre-adsorption and  $\text{N}_2$  purging. After the introduction of  $\text{NO} + \text{O}_2$ , the adsorbed  $\text{NH}_3$  species decreased in intensity and totally vanished after 10 min, followed by the appearance of nitrate species. The adsorbed  $\text{NH}_3$  species on  $\text{VO}_x/\text{CeO}_2(\text{S})$  could also participate in the SCR reaction, similar to  $\text{VO}_x/\text{CeO}_2(\text{P})$ .

**3.4.4 In situ DRIFTS of the reaction between  $\text{NH}_3$  species and pre-adsorbed  $\text{NO}_x$  species.** The catalysts were first treated with  $\text{NO} + \text{O}_2$  for 30 min, followed by  $\text{N}_2$  purging. When  $\text{NH}_3$  was introduced, the IR spectra were recorded as a function of time. For the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst (Fig. 10(A)), after  $\text{NO} + \text{O}_2$  pre-adsorption and  $\text{N}_2$  purging, the catalyst surface was covered with various nitrate species. When  $\text{NH}_3$  was introduced, the intensity of the bands attributed to monodentate nitrate and bridging nitrate species decreased slightly. The amount of bidentate nitrate species increased markedly, which may be due to the transformation of monodentate and bridging nitrate to bidentate nitrate. The changes in band intensities of nitrate species on  $\text{NO}_x$  pre-adsorbed catalysts during the introduction of  $\text{NH}_3$  are shown in Fig. S5.† The bands at 1425 and  $1158 \text{ cm}^{-1}$  attributed to adsorbed  $\text{NH}_3$  species appeared after  $\text{NH}_3$  was introduced. The adsorbed nitrate species could not easily react with adsorbed  $\text{NH}_3$ . This suggests that the adsorbed nitrate species were mostly inactive in the  $\text{NH}_3$ -SCR reaction.

For the  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalyst (Fig. 10(B)), similar bands ascribed to nitrate species were observed after  $\text{NO} + \text{O}_2$  adsorption and  $\text{N}_2$  purging. When  $\text{NH}_3$  was introduced, the intensity of bridging nitrate decreased slowly and the bands attributed to monodentate and bidentate nitrate species remained unchanged. Adsorbed  $\text{NH}_3$  species began to form on the  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalyst surface after 2 min upon  $\text{NH}_3$ .

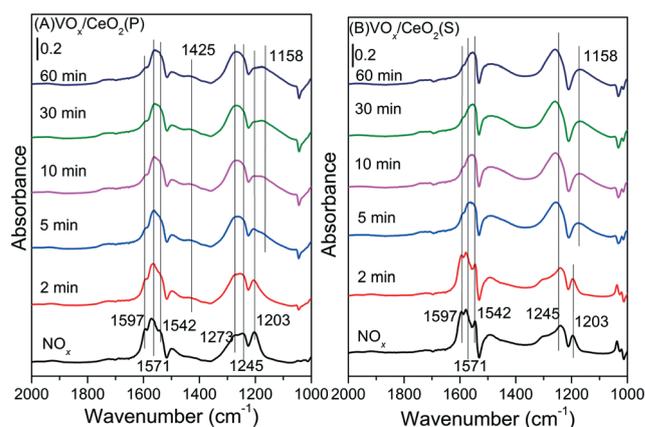


Fig. 10 *In situ* DRIFT spectra of  $\text{VO}_x/\text{CeO}_2(\text{P})$  (A) and  $\text{VO}_x/\text{CeO}_2(\text{S})$  (B) pretreated by exposure to 500 ppm  $\text{NO} + 5 \text{ vol.}\% \text{ O}_2$  followed by exposure to 500 ppm  $\text{NH}_3$  at  $200 \text{ }^\circ\text{C}$ .

introduction. The adsorbed nitrate could not easily take part in the  $\text{NH}_3$ -SCR reaction.

## 4. Discussion

### 4.1 The effect of preparation methods on catalytic activity

The effect of preparation methods on the catalytic activity of  $\text{VO}_x/\text{CeO}_2$  catalysts was investigated in detail in this study.  $\text{VO}_x/\text{CeO}_2$  prepared by the homogeneous precipitation method showed the highest SCR activity, and nearly 100%  $\text{NO}_x$  conversion plus 100%  $\text{N}_2$  selectivity was obtained above 200 °C. In addition,  $\text{VO}_x/\text{CeO}_2(\text{P})$  exhibited the strongest resistance to  $\text{H}_2\text{O}$  and  $\text{SO}_2$  in  $\text{NH}_3$ -SCR.

Based on the XRD results, the crystallinity of the  $\text{CeO}_2$  phase in the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst was higher than that in  $\text{VO}_x/\text{CeO}_2(\text{S})$ . However, the Raman spectra showed that the homogeneous precipitation method restrained the crystallization of  $\text{CeO}_2$  on the surface layer of the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst. The lower surface crystallinity signifies more defects on the catalyst surface and better dispersion of vanadium species, which could enhance catalytic activity. Higher surface vanadium concentration on the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst, as shown by XPS results, indicated more active sites and improved the  $\text{NH}_3$ -SCR performance.

In addition, the surface acidity of a catalyst plays an important role in the  $\text{NH}_3$ -SCR reaction.  $\text{VO}_x/\text{CeO}_2(\text{P})$  and  $\text{VO}_x/\text{CeO}_2(\text{S})$  showed similar specific surface areas, but the  $\text{NH}_3$  desorption amount from the former was much larger, indicating that the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst could provide more acid sites. This could result from the higher surface concentration of vanadium species, since acid sites are more prevalent on vanadium oxide than on cerium oxide. More acid sites on the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst could facilitate the adsorption and activation of  $\text{NH}_3$  during the catalytic reaction and thus enhance its catalytic activity in  $\text{NH}_3$ -SCR.

Furthermore, according to the literature,<sup>37,38</sup> vanadium oxide shows excellent  $\text{SO}_2$  resistance in  $\text{NH}_3$ -SCR. Therefore, a higher surface concentration of vanadium species on the catalyst surface could enhance  $\text{SO}_2$  resistance. The  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst showed higher catalytic activity in the presence of 100 ppm  $\text{SO}_2$  than  $\text{VO}_x/\text{CeO}_2(\text{S})$ .

### 4.2 SCR reaction mechanism

$\text{NH}_3$  could adsorb on  $\text{VO}_x/\text{CeO}_2(\text{P})$  and  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalysts to form  $\text{NH}_4^+$  and coordinated  $\text{NH}_3$ . When  $\text{NO}_x$  was introduced,  $\text{NH}_3$  adsorbed species disappeared quickly. Both  $\text{NH}_4^+$  and coordinated  $\text{NH}_3$  could react with  $\text{NO}_x$ . Monodentate, bridging and bidentate nitrates were deposited on the catalyst surface when  $\text{NO} + \text{O}_2$  were introduced. Adsorbed nitrate species were mostly inactive in the  $\text{NH}_3$ -SCR reaction. After  $\text{NH}_3$  was introduced, the number of monodentate and bridging nitrates reduced slightly, but the amount of bidentate nitrate increased. Gaseous  $\text{NO}$  mainly interacted with adsorbed  $\text{NH}_3$  species on  $\text{VO}_x/\text{CeO}_2$  catalysts to form an activated intermediate and subsequently decomposed to  $\text{N}_2$  and  $\text{H}_2\text{O}$  according to the Eley-Rideal mechanism.<sup>39</sup>

## 5. Conclusions

$\text{VO}_x/\text{CeO}_2$  catalysts exhibited excellent  $\text{NH}_3$ -SCR performance.  $\text{VO}_x/\text{CeO}_2$  prepared by a simple homogeneous precipitation method showed higher catalytic activity and better  $\text{H}_2\text{O}$  and  $\text{SO}_2$  resistance than catalysts prepared by other methods. As high as 93%  $\text{NO}_x$  conversion was obtained in the presence of 100 ppm  $\text{SO}_2$  for a 24 h test over the  $\text{VO}_x/\text{CeO}_2(\text{P})$  catalyst.

The weaker crystallinity of  $\text{CeO}_2$  in the surface layers of  $\text{VO}_x/\text{CeO}_2(\text{P})$  implied more defects on its surface and better dispersion of vanadium species than that on  $\text{VO}_x/\text{CeO}_2(\text{S})$ . The higher surface vanadium concentration led to more acid sites on  $\text{VO}_x/\text{CeO}_2(\text{P})$ , which can absorb and activate more  $\text{NH}_3$  species. All of these factors contributed to the higher SCR activity and  $\text{SO}_2$  resistance of  $\text{VO}_x/\text{CeO}_2(\text{P})$ . The  $\text{NH}_3$ -SCR reaction over  $\text{VO}_x/\text{CeO}_2(\text{P})$  and  $\text{VO}_x/\text{CeO}_2(\text{S})$  catalysts mainly followed the Eley-Rideal mechanism, in which gaseous  $\text{NO}$  reacted with adsorbed  $\text{NH}_3$  species to finally form  $\text{N}_2$  and  $\text{H}_2\text{O}$ .

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