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# Promoted dispersion and uniformity of active species on Fe–Ce–Al catalysts for efficient NO abatement†

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Fe–Ce–Al catalysts were synthesized by the co-precipitation method (labeled as Fe–Ce–Al–P), co-impregnation method (Fe–Ce–Al–I), and direct mixing method (Fe–Ce–Al–M), respectively, and used for effective removal of NO. The synthesized catalysts were characterized by many methods including N<sub>2</sub> physisorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD), H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR), high-resolution transmission electron microscopy (HR-TEM), and energy dispersive spectroscopy (EDS) mapping. The results show that the synthesis methods greatly influence the catalytic performance of catalysts. The Fe–Ce–Al–P catalyst prepared by the co-precipitation method yields the highest catalytic performance, while the Fe–Ce–Al–I and Fe–Ce–Al–M catalysts exhibit relatively low catalytic activity. The co-precipitation method can promote the accumulation and dispersion of more surface active species on the catalyst surface, and provide smaller particle size of active species and generate more uniform particle size distribution, while these characteristics can't be obtained by the co-impregnation method and direct mixing method. Moreover, the co-precipitation method could produce the highest surface area and enhanced redox ability and surface acidity of the catalyst, which resulted from the high dispersion and uniform distribution of surface active species. These may be the key factors to the superior catalytic performance of the Fe–Ce–Al–P catalyst.

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## 1. Introduction

Nitrogen oxides (NO<sub>x</sub>), as a typical pollutant from the combustion process, have caused severe problems in the environment and to human health.<sup>1</sup> To date, several methods and technologies have been developed to remove NO<sub>x</sub> and selective catalytic reduction (SCR) is proven to be the most effective route for NO abatement.<sup>2</sup> The key issue for SCR technology is the catalyst and the currently used catalysts for this process are V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> or V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub>.<sup>3</sup> Although the V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–TiO<sub>2</sub> (VWTi) catalyst system could yield high SCR catalytic activity, it also possesses inherent drawbacks, such as relatively narrow catalytic activity temperature window, the poisonous effect of VO<sub>x</sub> to the ecosystem and higher oxidation activity of SO<sub>2</sub> to SO<sub>3</sub>.<sup>4</sup> Due to this fact, many highly active and

environmentally friendly catalysts without VO<sub>x</sub> have been developed and may be an alternative route to solve these problems mentioned above.

According to this view, some transition-metal containing oxides, including FeO<sub>x</sub>, CuO<sub>x</sub>, MnO<sub>x</sub>, CeO<sub>x</sub>, and CrO<sub>x</sub>, have been designed for the replacement of the commercial SCR catalysts.<sup>5–9</sup> Among them, the Fe-containing catalysts have attracted special attention due to its better catalytic activity, favorable N<sub>2</sub> selectivity and nontoxicity.<sup>9,10</sup> And especially the bimetallic Fe catalysts, including Fe–Mn,<sup>11,12</sup> Fe–Ce,<sup>9,13</sup> Fe–Cu<sup>14</sup> and Fe<sub>x</sub>–W<sub>1–x</sub>O<sub>8</sub>,<sup>15</sup> exhibited superior catalytic activity for the SCR reaction. For the Fe–Ce catalysts, many researchers have widely studied this system from different levels and angles. Jiang *et al.* doped Ce onto Fe/β by a simple impregnation step and found Fe–Ce/β catalyst showed high catalytic activity and better hydrothermal stability.<sup>9</sup> Ma *et al.* supported Fe–Ce on carbon nanotube by an ethanol impregnation method and ascribed its excellent catalytic performance to the crystal CeO<sub>2</sub> and enriched chemisorbed oxygen of catalyst surface.<sup>16</sup> Zhang *et al.* synthesized Fe–S–Ce catalysts using the one-pot method and found the excellent SCR performance had a close relationship with the abundant chemisorbed oxygen and the enhanced surface acidity and redox property.<sup>17</sup> Previous studies for the Fe–Ce catalysts mainly focused on the Fe–Ce mixed metal oxides prepared by the one-pot method and supported Fe–Ce on H-

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$\beta$  zeolite and carbon nanotube, respectively, using the impregnation method. It is well known that the catalytic performance of catalysts greatly depends on the synthesis methods, support, precursors, oxidation state and crystallinity of metal oxides.<sup>18</sup> However, for the Fe–Ce–Al catalysts, the effect of catalysts synthesis methods on the catalytic activity is still lack of study, and the research on promoting the uniformity of particle size distribution and dispersion characteristics of surface active species by different synthesis methods to achieve superior catalytic performance is not systematically reported in the literature so far, especially the research on the mechanism of optimizing the physicochemical properties of catalyst by promoting the uniformity and dispersion of surface active species. Therefore, based on the discussion above, it is of great importance to reveal the intrinsic relationship among the component, the structure and the catalytic performance of catalyst resulted from different synthesis methods in the angle of promoting active species dispersion and uniformity on Fe–Ce–Al catalysts.

In the present work, the Fe–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts with the same Fe/Ce molar ratio were synthesized by three different synthetic strategies and used in the NH<sub>3</sub>–SCR reaction. The relationship between the physicochemical properties resulted from different synthesis methods and the excellent catalytic activity was explored *via* different characterization techniques, such as BET, XRD, H<sub>2</sub>–TPR, NH<sub>3</sub>–TPD, XPS, HR–TEM, and EDS mapping.

## 2. Materials and methods

### 2.1 Catalysts synthesis

**2.1.1 Co-precipitation method.** 18.04 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 38.78 g Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were added into 200 mL deionized water simultaneously and dissolved completely to get the mixed solution with the designed molar ratio of Fe : Ce being 1 : 2. And then, 25 g Al<sub>2</sub>O<sub>3</sub> power was added to the solution with magnetic stirring for 10 min at 50 °C. Later, the ammonia solution (wt 25%) was gradually added to with continuous stirring until the pH value reached 9–10. After stirring for 1.5 h, the resulting suspension was first dried at 120 °C for 12 h and then air-calcined at 450 °C for 5 h. And then, the calcined samples were compressed into tablet form and finally crushed and sieved to 30–60 mesh size for use. The sample was denoted as Fe–Ce–Al–P.

**2.1.2 Co-impregnation method.** The synthesis processes were the same as the co-precipitation method described above without adding the ammonia solution (wt 25%) to the solution. The sample was labeled as Fe–Ce–Al–I.

**2.1.3 Direct mixing method.** 3.56 g Fe<sub>2</sub>O<sub>3</sub>, 15.36 g CeO<sub>2</sub>, and 25 g Al<sub>2</sub>O<sub>3</sub> power were simultaneously added into 200 mL deionized water to get the solution with a molar ratio of Fe : Ce = 1 : 2. And then the solution was stirred for 10 min at 50 °C. The following processes were the same as the co-precipitation method mentioned above without adding the ammonia solution (wt 25%) to the solution. The sample was named as Fe–Ce–Al–M.

### 2.2 Catalyst characterization

N<sub>2</sub> adsorption–desorption was carried out at –196 °C on a Quantachrome Quadrisorb SI instrument.

X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (Smartlab 9, Japan) to study the crystal structure of the sample with CuK $\alpha$  radiation in the  $2\theta$  range from 10 to 90°.

X-ray photoelectron spectroscopy (XPS) analysis was performed to investigate the surface elements and chemical states of the samples on Thermo Fisher Scientific XPS (EXCALAB 250Xi) spectroscopy.

NH<sub>3</sub>–TPD and H<sub>2</sub>–TPR experiments were carried out on a Micromeritics Autochem 2920 II instrument to investigate the acidity and redox property of each studied sample. For the H<sub>2</sub>–TPR experiments, about 110 mg sample was used and pre-treated in N<sub>2</sub> at 200 °C for 1 h. And the data was recorded from 100 to 760 °C with a heating rate of 10 °C min<sup>–1</sup>. For the NH<sub>3</sub>–TPD experiments, about 200 mg sample was used and pre-treated with He at 450 °C for 1 h. And the TPD experiment was conducted from 100 to 800 °C with a heating rate of 10 °C min<sup>–1</sup>.

HR–TEM images and EDS mappings were obtained using a JOEL JEM-2100 electron microscope operated at 200 kv to investigate the microstructure of the samples and the elements dispersion.

### 2.3 Catalytic activity measurement

SCR activity measurement was accomplished in a fixed bed reactor using a 5 mL sample (30–60 mesh). The simulated flue gas was composed of NH<sub>3</sub> (500 ppm), NO (500 ppm), 3% O<sub>2</sub> and balance N<sub>2</sub>. The reactions were executed with a total gas flow rate of 1.5 L min<sup>–1</sup>. All the data were measured online by a flue gas analyzer (rbr ECOM–J2KN, Germany) under steady state. The NO<sub>x</sub> conversion was calculated *via*:

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

## 3. Results and discussions

### 3.1 Catalytic performance

The NO conversion of Fe–Ce–Al catalysts prepared by different methods is shown in Fig. 1. It can be seen that the Fe–Ce–Al–M catalyst exhibits the lowest NO conversion, which is less than 45.6% at 120–360 °C. And the SCR catalytic activity of the Fe–Ce–Al–I catalyst is greatly improved compared with that of the Fe–Ce–Al–M catalyst. With the increase of reaction temperature, the NO conversion of Fe–Ce/Al<sub>2</sub>O<sub>3</sub>–I catalyst gradually increases from 26.2% to 88.8% at 120–330 °C and then decreases to 88% at 360 °C. For the Fe–Ce–Al–P catalyst, it yields the highest SCR activity in the whole temperature range. More than 96% NO conversion can be obtained in 270–360 °C. These three catalysts prepared by different methods have the same chemical compositions but show a significant difference in catalytic activity. The results demonstrate that the preparation methods



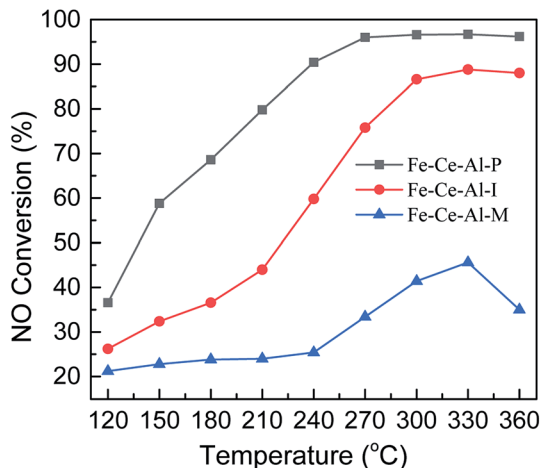


Fig. 1 NO conversion of catalysts prepared by different methods.

have a great effect on its catalytic activity. Furthermore, as shown in Fig. S1,<sup>†</sup> after a 6 h long reaction at 330 °C, the Fe-Ce-Al-P catalyst still exhibits the best catalytic activity, suggesting the superior activity of the Fe-Ce-Al-P catalyst. The effect of different physicochemical properties of catalysts resulted from the preparation methods on the catalytic performance will be systematically investigated using various characterization technique in the following sections.

### 3.2 Catalyst characterization

**3.2.1 BET surface area and pore size measurements.** Table 1 displays the BET surface area, pore volume and pore diameter of the studied samples. Obviously, the  $\text{Al}_2\text{O}_3$  support exhibits the largest BET surface area ( $168.30 \text{ m}^2 \text{ g}^{-1}$ ) and pore volume ( $0.27 \text{ mm}^3 \text{ g}^{-1}$ ). After the addition of Fe and Ce, the BET surface areas and pore volumes of the studied three samples are decreased due to the dispersion of active species and the sequence is ranked by Fe-Ce-Al-P > Fe-Ce-Al-I > Fe-Ce-Al-M, which is highly consistent with the catalytic performance of catalysts. It indicates that the dispersion of Fe and Ce species on the three catalysts prepared by different methods is different. The larger surface area could provide more surface active sites to promote the adsorption capacity. And big pore volumes could favor the spread of the reaction intermediates and reactant gas.<sup>19</sup> All of these will make the reaction process more efficient and lead to excellent catalytic performance.

Table 1 BET surface area and pore structure results of different samples

Catalysts	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	Pore volume ( $\text{mm}^3 \text{ g}^{-1}$ )	Pore diameter (nm)
Fe-Ce-Al-P	122.30	0.23	3.72
Fe-Ce-Al-I	94.88	0.20	3.51
Fe-Ce-Al-M	94.09	0.17	3.94
$\text{Al}_2\text{O}_3$	168.30	0.27	3.51

**3.2.2 X-ray powder diffraction (XRD) analysis.** The structural characteristic of different catalysts was investigated by XRD and the results are shown in Fig. 2. For all the Fe-Ce-Al catalysts, no visible characteristic peaks of Fe species can be observed, indicating the iron species are highly dispersed on the surface of catalysts or exist as amorphous. While several strong characteristic peaks attributed to the  $\text{CeO}_2$  phase are detected on the catalysts and the same phenomenon can be seen in the XRD patterns of the catalysts after the SCR reaction displayed in Fig. S2.<sup>†</sup> Compared with those of the Fe-Ce-Al-M catalyst, the peak intensities of the crystal  $\text{CeO}_2$  phase are significantly reduced and the peak shapes are broadened on the Fe-Ce-Al-I and Fe-Ce-Al-P catalysts, suggesting that the crystallinity of catalyst is reduced and the coalescence of particles is inhibited.<sup>19,20</sup> The results discussed above clearly indicate that the preparation method has a significant effect on the crystal structure of catalysts. Moreover, the particle size of the catalyst is calculated with the Scherrer equation and the corresponding results are listed in Table 2. It turns out that the crystallite size of the main crystal  $\text{CeO}_2$  phase is calculated to be 6.8, 7.4, and 59.6 nm for the Fe-Ce-Al-P, Fe-Ce-Al-I, and Fe-Ce-Al-M catalyst, respectively. And compared with that of Fe-Ce-Al-M catalyst, the full-width-half-maximum (FWHM) of crystal  $\text{CeO}_2$  peak over the Fe-Ce-Al-P and Fe-Ce-Al-I catalysts is greatly broadened. It demonstrates that there is a strong interaction between Ce and Fe and this effect inhibits the growth of the crystalline  $\text{CeO}_2$  phases on one hand; and on the other hand, compared with direct mixing method, the co-precipitation method and co-impregnation method could lead to different degrees of local distortion and result in different physical properties of  $\text{CeO}_2$  such as the crystallite size.<sup>9,19,21</sup> Fe-Ce-Al-P catalyst generates the smallest particle size and would lead to better dispersion of active species. And the results of this effect are that the specific surface area of the catalyst is enlarged and therefore the catalytic performance is enhanced.

**3.2.3 X-ray photoelectron spectroscopy (XPS) analysis.** XPS analysis was used to explore the valence states and chemical

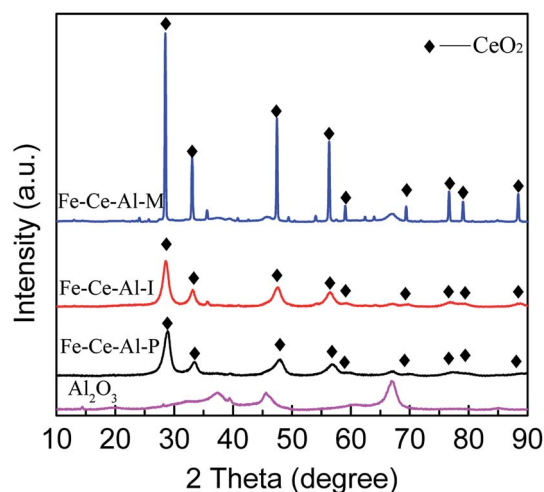


Fig. 2 XRD patterns of different Fe-Ce-Al catalysts and  $\text{Al}_2\text{O}_3$  support.



Table 2 Crystalline sizes of different catalysts

Catalysts	2 Theta (°)	Area	FWHM (rad)	D (nm)
Fe-Ce-Al-P	28.68	181 128	1.22	6.8
Fe-Ce-Al-I	28.56	173 729	1.11	7.4
Fe-Ce-Al-M	28.47	269 135	0.17	59.6

Table 3 XPS results of the Fe-Ce-Al catalysts

Catalysts	Binding energy (eV)			Surface atomic ratio (%)		
	Fe 2p		O 1s			
	Fe <sup>3+</sup>	Fe <sup>2+</sup>	O <sub>α</sub>	Fe <sup>3+</sup> /(Fe <sup>3+</sup> + Fe <sup>2+</sup> )	Ce <sup>3+</sup> /(Ce <sup>3+</sup> + Ce <sup>4+</sup> )	O <sub>α</sub> /(O <sub>α</sub> + O <sub>β</sub> )
Fe-Ce-Al-P	711.5	710.5	531.8	68.62	37.91	42.72
Fe-Ce-Al-I	712.5	710.7	531.8	38.47	19.16	27.99
Fe-Ce-Al-M	713.5	710.8	532.6	18.24	17.29	20.28

components of the samples and the results are displayed in Fig. 3 and Table 3.

The Fe 2p spectra for the investigated catalysts are shown in Fig. 3(a). Two characteristic peaks located at about 710.8–711.3 eV and 723.8–725 eV could be ascribed to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>, respectively. And the spectra of Fe 2p<sub>3/2</sub> can be fitted into two sub-bands. The peak locates at about 710.5 eV is attributed to Fe<sup>2+</sup>, while the peak at about 712.5 eV is ascribed to the Fe<sup>3+</sup>, indicating the coexistence of FeO and Fe<sub>2</sub>O<sub>3</sub> on the surface of studied samples.<sup>22</sup> Moreover, compared with that of the Fe-Ce-Al-I and Fe-Ce-Al-M catalysts, the binding energies for Fe<sup>2+</sup> and Fe<sup>3+</sup> over Fe-Ce-Al-P catalyst are shifted to lower values, indicating the Fe species on the surface of Fe-Ce-Al-P catalyst prepared by co-precipitation method are more active, which will help to promote the catalytic performance.<sup>7</sup> The relative

proportions of Fe<sup>3+</sup> and Fe<sup>2+</sup> were calculated by the peak area of Fe 2p<sub>3/2</sub> for Fe<sup>3+</sup> and Fe<sup>2+</sup> (listed in Table 3). The Fe<sup>3+</sup>/(Fe<sup>3+</sup>+Fe<sup>2+</sup>) over the Fe-Ce-Al-P catalyst is 68.62%, while it is only 38.47% and 18.24% for the Fe-Ce-Al-I and Fe-Ce-Al-M catalysts, respectively. It indicates that the Fe-Ce-Al-P catalyst prepared by the co-precipitation method can generate more Fe<sup>3+</sup> species on the catalyst surface. And more Fe<sup>3+</sup> sites could promote the conversion of NO to NO<sub>2</sub> during the SCR reaction and thus enhance the catalytic activity through the “Fast SCR” reaction.<sup>22,23</sup>

The XPS spectra of the Ce 3d for the three catalysts are displayed in Fig. 3(b), which all can be fitted into peaks labeled as u, u<sub>1</sub>, u<sub>2</sub>, u<sub>3</sub>, v, v<sub>1</sub>, v<sub>2</sub>, and v<sub>3</sub>, respectively. The peaks denoted as

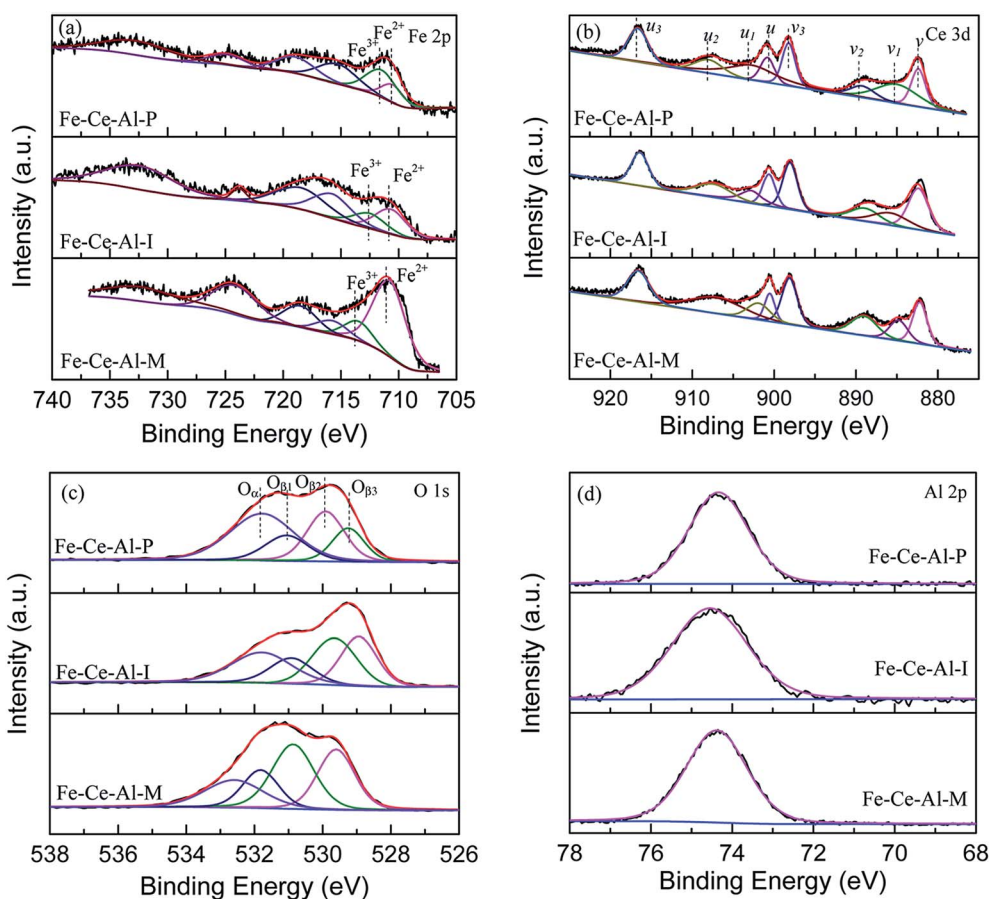


Fig. 3 XPS spectra of (a) Fe 2p, (b) Ce 3d, (c) O 1s and (d) Al 2p for Fe-Ce-Al catalysts.





$u_1$  and  $v_1$  are attributed to the  $Ce^{3+}$ , while others are ascribed to  $Ce^{4+}$ , suggesting the coexistence of the  $Ce^{4+}$  and  $Ce^{3+}$  on the catalyst surface. In addition, the  $Ce^{3+}/(Ce^{4+} + Ce^{3+})$  ratio over the three samples is decreased as follows: Fe–Ce–Al–P (37.91%) > Fe–Ce–Al–I (19.16%) > Fe–Ce–Al–M (17.29%). It fully indicates that the contents of  $Ce^{3+}$  species are closely related to the preparation methods of the catalysts and more  $Ce^{3+}$  species can be generated on the catalyst surface by the co-precipitation method. On one hand, more  $Ce^{3+}$  species can generate more charge imbalance and oxygen vacancies on the catalyst surface, leading to the enhancement of surface chemisorbed oxygen and therefore facilitation of NO oxidation,<sup>21,24,25</sup> on the other hand, more surface  $Ce^{3+}$  species can promote the adsorption of NO and  $NH_3$ , and thus contribute to the enhancement of catalytic activity.<sup>26,27</sup> These may be the reasons for the superior catalytic activity of the Fe–Ce–Al–P catalyst.

The O 1s spectra of the studied samples after peak fitting is shown in Fig. 3(c) can be separated into two groups. The peak  $O_\alpha$  located at about 532 eV is assigned to the surface adsorbed oxygen, such as  $O_2^{2-}$ , OH, and  $O^-$  species;<sup>1,28</sup> while the peak  $O_\beta$  centered at about 530 eV is ascribed to the lattice oxygen.<sup>29</sup> After further peak fitting, the peak  $O_\beta$  can be divided into three peaks labeled as  $O_{\beta 1}$ ,  $O_{\beta 2}$  and  $O_{\beta 3}$ , respectively. The  $O_{\beta 1}$  recorded at about  $529.3 \pm 0.3$  eV is originated from the  $CeO_2$ ,<sup>30–32</sup> and the  $O_{\beta 2}$  located at  $529.9 \pm 0.3$  eV can be attributed to oxygen species corresponding to the  $Fe_2O_3$ ,<sup>33–36</sup> while the  $O_{\beta 3}$  at about 531 eV can be assigned to the Al–O bonds of  $Al_2O_3$ .<sup>37–42</sup> Additionally, the sequence of the relative amount of  $O_\alpha$  is ranked by Fe–Ce–Al–P > Fe–Ce–Al–I > Fe–Ce–Al–M catalyst. As the most active catalyst, the Fe–Ce–Al–P catalyst is provided with the highest content of surface adsorbed oxygen with the lowest binding energy, implying the improved oxygen mobility, which is beneficial to promote SCR performance.

The XPS spectra of Al 2p for different samples are detailed in Fig. 3(d). The binding energies of the Al 2p are all centered at about  $74.4 \pm 0.1$  eV. The basically unchanged binding energies of Al 2p demonstrates that the synergistic effect between Fe and Ce species is dominant over the catalysts.

Based on the XPS discussion above, the Fe–Ce–Al–P catalyst possesses the highest content of  $Fe^{3+}$  and  $Ce^{3+}$ , the redox couples between  $Fe^{3+}/Fe^{2+}$  and  $Ce^{4+}/Ce^{3+}$  may enhance the redox cycle, which would accelerate the electron transfer and promote the generation of oxygen vacancy, and therefore facilitate the catalytic performance.<sup>29,43</sup>

**3.2.4  $NH_3$ -TPD analysis.** The surface acidity of catalysts was determined by the  $NH_3$ -TPD experiment and the corresponding results are exhibited in Fig. 4. All the  $NH_3$ -TPD curves of catalysts after peak fitting contain six  $NH_3$  desorption peaks within the temperature of 100–800 °C, which are related to weak acids (<300 °C), medium acids (300–500 °C), and strong acids (>500 °C), respectively.<sup>4,22,44</sup> For comparison, the total amount of acidity of catalysts is calculated and the total acidity of Fe–Ce–Al–P, Fe–Ce–Al–I, and Fe–Ce–Al–M catalysts is 0.431, 0.386, and 0.354 mmol g<sup>−1</sup>, respectively. Despite having the same components, the surface acidity obviously differs on each catalyst with different preparation methods, suggesting the co-precipitation treatment could enhance the total amount of acidity,

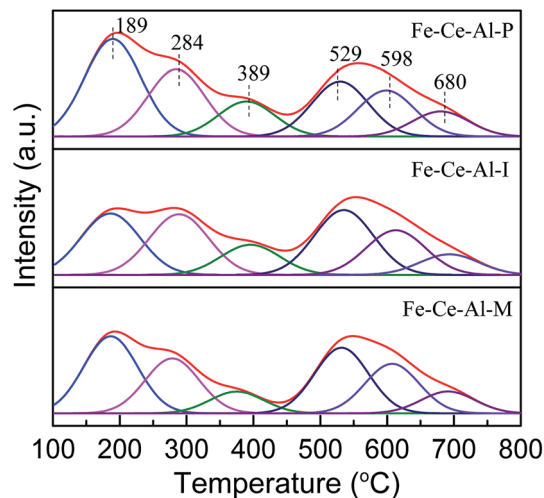


Fig. 4  $NH_3$ -TPD profiles of different catalysts.

especially the weak and moderate acidity (depicted in Table 4). As expected, the SCR activity is highly consistent with the order of the total amount of acidity. Based on the BET, XRD, and XPS results, the co-precipitation method can promote the dispersion of active species and generate small particle size, and thus result in a large surface area. Therefore, the Fe–Ce–Al–P catalyst could provide more acid sites and promote the adsorption of  $NH_3$  on the catalyst surface, thereby could exhibit superior catalytic activity.

**3.2.5  $H_2$ -TPR analysis.** The redox properties of catalysts were evaluated by  $H_2$ -TPR analysis and the results are depicted in Fig. 5. It can be clearly seen that all  $H_2$ -TPR profiles of the catalysts exhibit five reduction peaks after peaking fitting in the whole temperature range. For the Fe–Ce–Al–P catalyst, the reduction peaks at 236 and 312 °C are assigned to the reduction process of chemisorbed oxygen and  $Fe_2O_3 \rightarrow Fe_3O_4$ .<sup>16</sup> And the peaks featured at 446 °C is associated with the reduction of the surface  $CeO_2$ .<sup>2,16</sup> While the reduction peaks at high temperatures (556 and 621 °C) are assigned to the reduction of  $Fe_3O_4 \rightarrow FeO$  and the  $FeO \rightarrow Fe$  overlap with those originating from the reduction of bulk  $CeO_2$ , respectively.<sup>2,16</sup> For the profiles of the Fe–Ce–Al–I catalyst, the reduction behavior is similar to that of the Fe–Ce–Al–P catalyst but the corresponding reduction peaks of Fe and Ce species shift towards higher temperatures. And this reduction characteristics are more pronounced on the Fe–Ce–Al–M catalyst in the low temperature (<500 °C). For comparison, the total consumption of  $H_2$  was calculated and

Table 4 Quantitative data of the  $NH_3$ -TPD profiles of catalysts

Catalysts	Acidity (mmol g <sup>−1</sup> )			
	Weak	Moderate	Strong	Total
Fe–Ce–Al–P	0.218	0.046	0.167	0.431
Fe–Ce–Al–I	0.167	0.041	0.178	0.386
Fe–Ce–Al–M	0.161	0.026	0.167	0.354



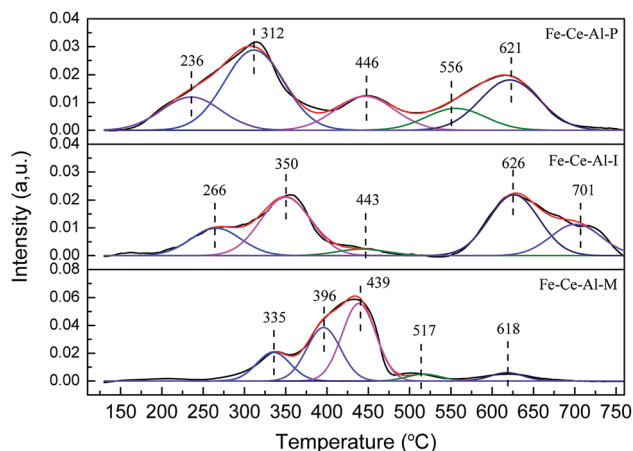


Fig. 5 H<sub>2</sub>-TPR profiles of different catalysts.

the data are as follows: Fe-Ce-Al-P ( $0.69 \text{ mmol g}^{-1}$ ) > Fe-Ce-Al-I ( $0.43 \text{ mmol g}^{-1}$ ) > Fe-Ce-Al-M ( $0.42 \text{ mmol g}^{-1}$ ). These results indicate that the Fe-Ce-Al-P catalyst yields the best redox ability, while that of the Fe-Ce-Al-I and Fe-Ce-Al-M catalyst is relatively reduced at low temperature. It is accepted that a change for the reduction peak position can be affected by many factors, such as particle sizes, structural defects, the content of surface oxygen and phase component.<sup>45</sup> Based on the XPS and XRD results, it may be due to the fact that the Fe-Ce-

Al-P catalyst has smaller particle sizes and better dispersion of active species, and higher surface oxygen content. Therefore the catalyst can exhibit enhanced redox ability and yield superior catalytic performance.

**3.2.6 HR-TEM analysis.** The micrographs and size distribution of different samples were obtained by HR-TEM analysis and the results of different scales and particle size distribution are shown in Fig. 6 and S3.† For the Fe-Ce-Al-P catalyst, it consists of uniform nanoparticles with the average particle size of 7.59 nm and displays well dispersion; and the shape of the particles for Fe-Ce-Al-I catalyst are irregularly containing some long strips particles. The average particle size is calculated to be 12.00 nm and some nanoparticles exist slight surface agglomeration. For the Fe-Ce-Al-M catalyst, the particle size distribution is extremely irregular and some large particles (>200 nm) could be observed, suggesting the poor dispersed nature of Fe and Ce species. Moreover, the resulting HR-TEM images of three catalysts shown in Fig. S4† exhibit the lattice fringes with interplanar distances of 0.31 nm corresponding to (1 1 1) planes of bulk CeO<sub>2</sub>.<sup>46</sup> These results are well consistent with the XRD results and demonstrate that the particle size and dispersion of active species are greatly dependent on the catalyst preparation method. The Fe-Ce-Al-P catalyst prepared by the co-precipitation method can generate better dispersion of active species and more uniform size distribution of nanoparticles. In general, the smaller particle size and better dispersion of active species will lead to better catalytic performance. On one hand,

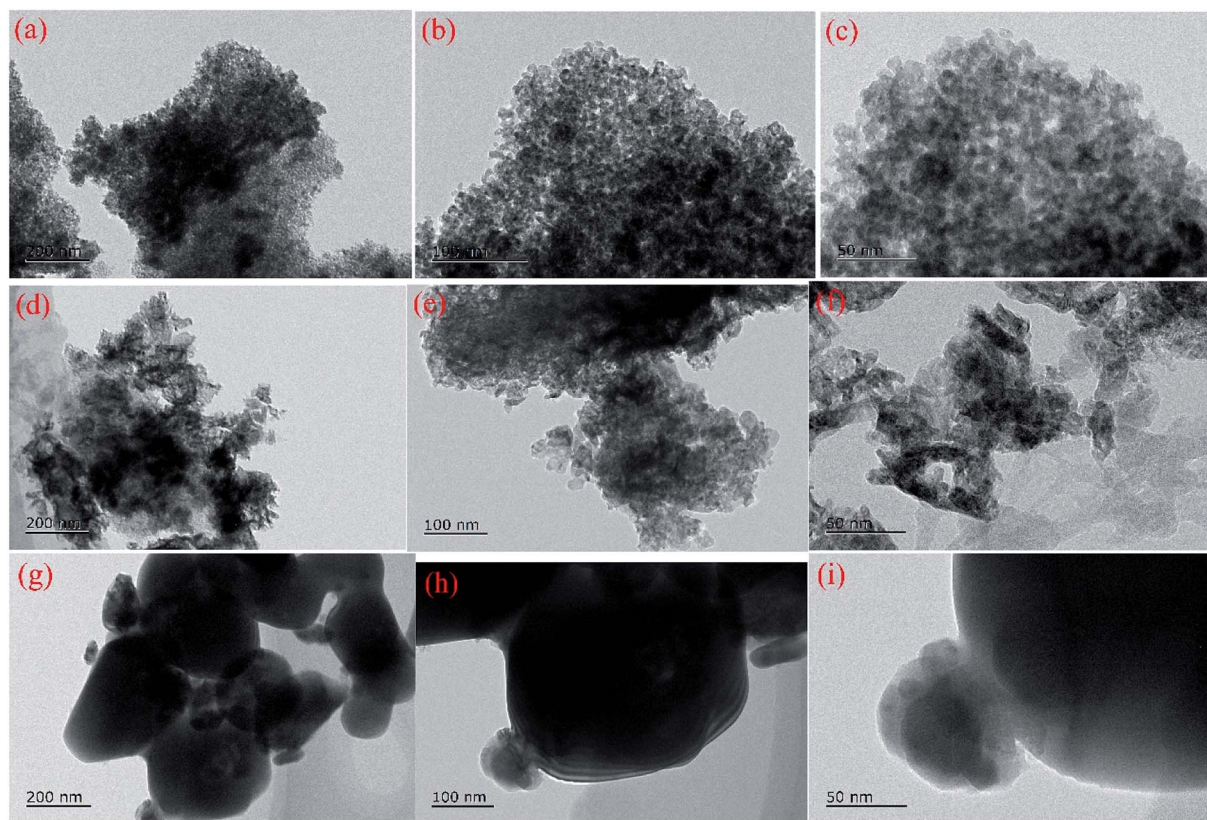


Fig. 6 TEM profiles of different catalysts (a–c) Fe-Ce-Al-P, (d–f) Fe-Ce-Al-I, and (g–i) Fe-Ce-Al-M.





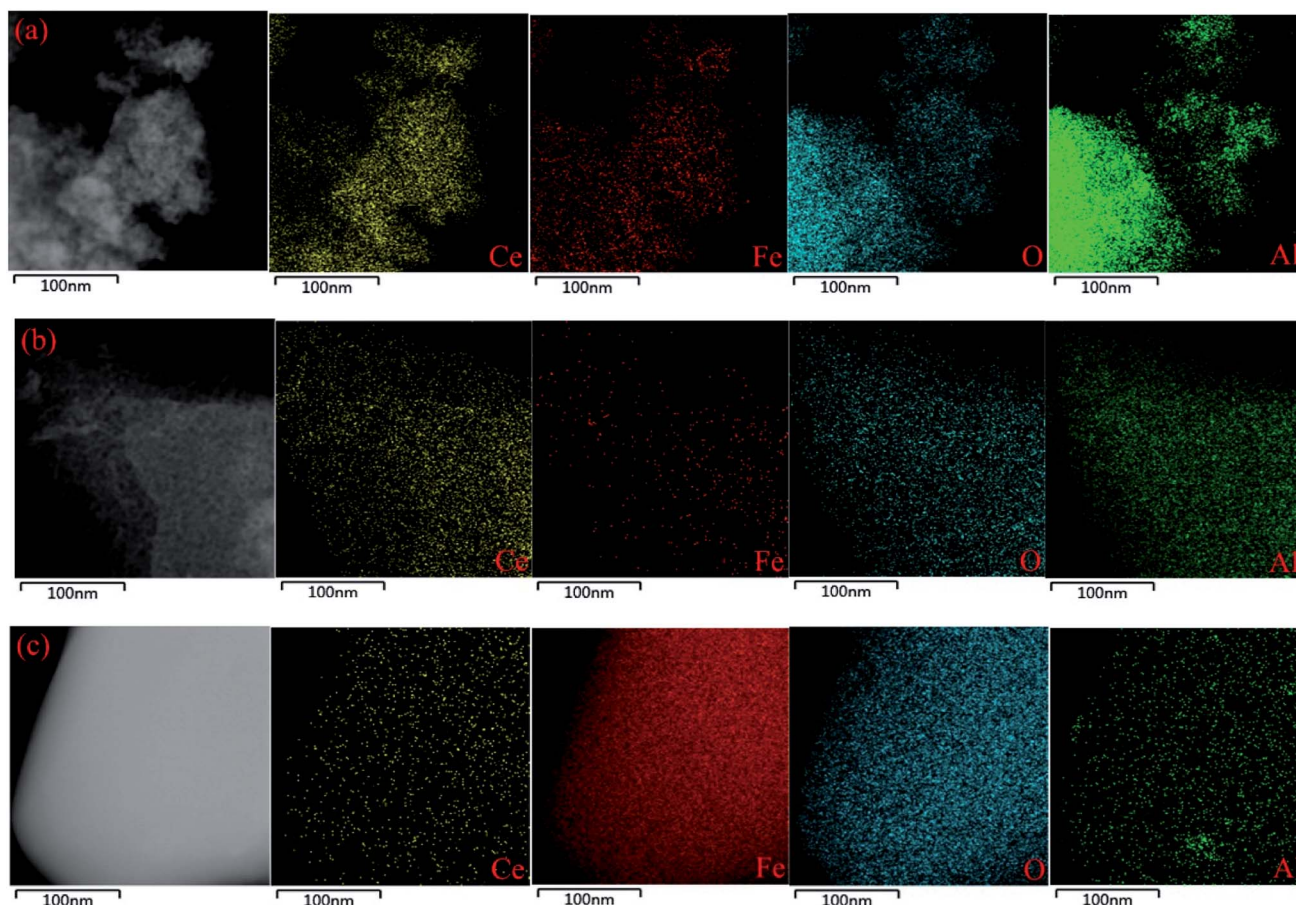


Fig. 7 TEM-EDS mapping results of different catalysts: (a) Fe–Ce–Al–P, (b) Fe–Ce–Al–I, and (c) Fe–Ce–Al–M.

the smaller particle size and better dispersion will generate a bigger surface area and thus provide more active sites. Therefore, more reactant gas molecule can be adsorbed in the catalyst surface and promote the catalytic performance; on the other hand, the redox ability of catalyst plays an important role in the SCR reaction. The redox ability of catalyst can be enhanced by smaller particle size and better dispersion of active species and thus will contribute to the enhanced the catalytic activity of the catalyst. In short, the co-precipitation method could generate smaller particle size and high dispersion of active species and therefore could exhibit superior catalytic performance.

**3.2.7 EDS mapping analysis.** EDS mapping was carried out to investigate different elements dispersion of catalysts and provide further evidence of different dispersion of active species over Fe–Ce–Al catalysts as depicted in Fig. 7. For the Fe–Ce–Al–P catalyst, the colored dots representing the concentration of Fe, Ce, and O elements, respectively, are dispersed highly and uniformly on the sample surface, while this phenomenon is not present in the Fe–Ce–Al–I and Fe–Ce–Al–M catalysts. Compared with that of the Fe–Ce–Al–P catalyst, the Fe–Ce–Al–I and Fe–Ce–Al–M catalyst exhibit poor dispersion and uniformity of active species. It can be seen from Fig. 7(b) and (c) that less Fe is dispersed on the Fe–Ce–Al–I catalyst surface compared to other

elements, while Ce exhibits poor dispersion on the Fe–Ce–Al–M catalyst surface and serious Fe aggregation occurs on its surface. These results demonstrate that the dispersion of active species on the surface of the Fe–Ce–Al–P catalyst is significantly better than that of Fe–Ce–Al–I and Fe–Ce–Al–M catalyst. Moreover, the SEM-EDS mapping results of the catalysts after the SCR reaction shown in Fig. S5† demonstrate that the Fe–Ce–Al–P catalyst still possesses the best dispersion of active species. On the basis of the characterization results of XRD, TEM, and EDS mapping, it can draw the conclusion that the co-precipitation method could inhibit the crystallinity of particles and improve the dispersion of active species compared with the other two methods, and therefore promote the catalytic activity of the catalyst.

## 4. Conclusion

In this work, Fe–Ce–Al catalysts were prepared by three different methods and the synthesis methods have a direct impact on the catalytic performance of catalysts. The Fe–Ce–Al–P catalyst prepared by the co-precipitation method yields the highest catalytic performance, while the Fe–Ce–Al–I and Fe–Ce–Al–M catalyst exhibit relatively low denitration efficiency. Compared with that of Fe–Ce–Al–I and Fe–Ce–Al–M catalyst, the Fe–Ce–Al–



P catalysts before and after the reaction possess the best dispersion of active species and more surface active species are accumulated on the surface of Fe–Ce–Al–P catalyst. And the Fe–Ce–Al–P catalyst could provide smaller particle sizes of active species and generate more uniform particle sizes distribution, all mentioned above may be the key factors to the superior catalytic performance. Moreover, the co-precipitation method could produce the highest surface area and the enhanced redox ability and surface acidity of the catalyst due to the high dispersion and uniform distribution of surface active pieces, and these characteristics will also directly contribute to the superior catalytic performance of Fe–Ce–Al–P catalyst.

## Conflicts of interest

There are no conflicts to declare.

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