




Cite this: *RSC Adv.*, 2019, 9, 15791

## N-doped graphene/CoFe<sub>2</sub>O<sub>4</sub> catalysts for the selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub>

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In this paper, CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts and N-doped graphene/CoFe<sub>2</sub>O<sub>4</sub> (CoFe<sub>2</sub>O<sub>4</sub>/graphene-N) catalysts were prepared using the hydrothermal crystallization method for the selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub>. The results of the test showed that CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts exhibited the best denitrification activity when the loading was at 4% and the conversion rate of NO<sub>x</sub> reached 99% at 250–300 °C. CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts presented a better denitrification activity at low temperature than CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts, and the conversion rate of NO<sub>x</sub> reached more than 95% at 200–300 °C. The intrinsic mechanism of CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts in promoting SCR activity was preliminarily explored. The physicochemical properties of the samples were characterized using XRD, TEM, N<sub>2</sub> adsorption, XPS, NH<sub>3</sub>-TPD, and H<sub>2</sub>-TPR. The results indicated that nitrogen doping can improve the dispersion of CoFe<sub>2</sub>O<sub>4</sub>, and it also increased the acidic sites and the redox performance conducive to improving the denitrification activity of the catalysts. In addition, CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts demonstrated a better resistance to water and sulfur than CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts.

Received 1st April 2019  
 Accepted 14th May 2019

DOI: 10.1039/c9ra02456e

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### 1. Introduction

Nitrogen oxide (NO<sub>x</sub>) is one of the typical atmospheric pollutants.<sup>1</sup> Selective catalytic reduction (SCR) is an effective method to control the emission of nitrogen oxides from coal-fired power plants.<sup>2</sup> At present, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts are still widely used in the denitrification process of coal-fired boilers and power plants. However, there are many disadvantages in practical applications, such as high running temperature, poor sulfur and water resistance, and short service life.<sup>3</sup> Therefore, the development of high activity denitrification catalysts at a low temperature is of great significance for environmental protection.

In recent years, iron-based catalysts have been widely used in SCR because of their fine catalytic performance, such as Fe/ZSM-5,<sup>4</sup> Fe/MCM-56,<sup>5</sup> Co-Fe,<sup>6</sup> Fe-Mn,<sup>7</sup> and Co<sub>3</sub>O<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub>@-SiO<sub>2</sub>@Au.<sup>8</sup> Among them, Spinel ferrite AFe<sub>2</sub>O<sub>4</sub> (A = Zn, Ni, Co, Mn) has the advantages of good chemical stability, high mechanical strength and excellent electromagnetic properties.<sup>9–11</sup> Kennedy *et al.* found that the photocatalytic degradation rate of Rhodamine B by Co<sub>0.6</sub>Mg<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> reached 99.5%.<sup>12</sup> Wang

*et al.* found that the photochemical degradation ability of CoFe<sub>2</sub>O<sub>4</sub>/MoS<sub>2</sub> nanocomposites prepared for organic dyes reached 94.9%.<sup>13</sup> The Co<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> nanocomposite studied by Das and co-workers exhibits good photocatalytic properties.<sup>14</sup> Graphene (GE) has been widely used as a carrier to improve the performance of catalysts due to its large specific surface area, high electron mobility and stable chemical properties.<sup>15,16</sup> Yao *et al.* found that CoFe<sub>2</sub>O<sub>4</sub>/graphene has better catalytic activity than CoFe<sub>2</sub>O<sub>4</sub> in phenol degradation.<sup>17</sup> Bian *et al.* found that CoFe<sub>2</sub>O<sub>4</sub>/graphene nanocomposites exhibit excellent catalytic activity in redox reactions.<sup>18</sup>

N-doped mesoporous carbon materials have been widely used in catalytic reactions. The modification of mesoporous carbon by incorporating nitrogen leads to the better particle dispersity, but also probably disturbs the electronic structure of carbon solids owing to the formation of a semiconductor-like energy gap.<sup>19</sup> To the best of our knowledge, the research of N-doped graphene/CoFe<sub>2</sub>O<sub>4</sub> (CoFe<sub>2</sub>O<sub>4</sub>/graphene-N) for NH<sub>3</sub>-SCR has been rarely reported. In this paper, graphene as catalysts carrier was used to prepare CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts for NH<sub>3</sub>-SCR reaction. The proper proportion of CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts was determined, and the effect of nitrogen doped on the denitrification performance of CoFe<sub>2</sub>O<sub>4</sub>/graphene catalyst was also investigated. The mechanism of CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalyst in promoting SCR activity was preliminarily explored, which provided a theoretical basis for the practical application of AFe<sub>2</sub>O<sub>4</sub> catalysts in NH<sub>3</sub>-SCR reaction.

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## 2. Experimental

### 2.1 Catalysts preparation

**2.1.1 Preparation of GO.** Graphene oxide was prepared using the Hummers' method.<sup>20</sup> The preparation process was as follows: 5 g of graphite powder, 2.5 g of sodium nitrate and 115 ml of concentrated sulfuric acid were firstly added to a three-necked flask placed in an ice water bath for stirring, and after being uniformly mixed, 15 g of potassium permanganate was added. The mixture was kept in the ice-water bath for 2 hours, and then transferred from the flask into the thermostat water bath again, and stirred for 30 min at 35 °C. Transfer the mixture in the three-necked flask into an ice water bath and then add 230 ml of deionized water. Finally, react at a constant temperature of 98 °C for 20 min. The reaction mixture was then cooled down naturally to room temperature. Subsequently, the hydrogen peroxide (50 ml) was added and stirred for 10 min. Wash and dry with HCl and deionized water, respectively.

**2.1.2 Preparation of CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts.** The CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts was prepared by the hydrothermal method.<sup>21</sup> 0.12 g GO was added to 60 ml anhydrous alcohol under ultrasonic for 30 min, as solution A. Another solution was to add a certain amount of cobalt nitrate and ferric nitrate to 20 ml absolute alcohol, namely solution B. Solution B was then added to solution A, and stirred for 30 minutes; after that, 2.16 g sodium acetate was added to continue stirring for 30 minutes, by then crystallized at 200 °C for 12 hours. In the meantime, the loads of 1CoFe<sub>2</sub>O<sub>4</sub>/graphene, 4CoFe<sub>2</sub>O<sub>4</sub>/graphene, 7CoFe<sub>2</sub>O<sub>4</sub>/graphene and 11CoFe<sub>2</sub>O<sub>4</sub>/graphene were prepared by changing the amount of cobalt nitrate and ferric nitrate added respectively. Adding solution B into A and adding 1 ml ammonia to prepare CoFe<sub>2</sub>O<sub>4</sub>/graphene-N, the preparation process is the same as above.

### 2.2 Evaluation of denitrification activity of the catalysts

The denitrification activity of the catalysts was tested with Shanghai Jiangke QJK45 denitrification experimental facility with 0.3 g catalysts. N<sub>2</sub> was used as balanced gas; NH<sub>3</sub> 500 ppm; NO 500 ppm; SO<sub>2</sub> 100 ppm; O<sub>2</sub> 5%; H<sub>2</sub>O 3%; the total gas flow was 100 ml min<sup>-1</sup>; the reaction temperature was 150–400 °C. The conversion rate of NO<sub>x</sub> was calculated according to the

content of NO<sub>x</sub> at the inlet and outlet at 150, 200, 250, 300, 350 and 400 °C respectively. The NO<sub>x</sub> content of the inlet gas was marked as [C<sub>NO<sub>x</sub></sub>]<sub>in</sub>, and the NO<sub>x</sub> content of the outlet gas was marked as [C<sub>NO<sub>x</sub></sub>]<sub>out</sub>. NO<sub>x</sub> conversion rate is calculate as:

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

### 2.3 Catalysts characterization

The crystal structure of the catalysts was characterized by Smart lab X-ray diffraction (XRD) of Nippon Science Corporation, with a scanning range of 5–80 degree, an operating current of 200 mA and an operating voltage of 45 kV. Hitachi H-7650 transmission electron microscopy (TEM) was used to characterize the microstructures of the samples (resolution 0.2 nm, acceleration voltage 40–120 kV, magnification 60 000×). The specific surface area, pore size distribution and pore volume of the catalysts was characterized by Autosorb IQ of Conta Instruments Company, USA. Thermo Fisher's ESCALAB250XI X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemical composition and the chemical state of each element. The surface acidity of the catalysts was characterized by temperature programmed desorption (NH<sub>3</sub>-TPD) of AutoChem 2920 NH<sub>3</sub>, an American company. AutoChem 2920 H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) was used to characterize and analyze the redox performance of the catalysts.

## 3. Results and discussion

### 3.1 Structure and microstructure analysis of catalysts

Fig. 1 shows the XRD patterns of the graphene oxide (GO), CoFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>/graphene, and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N. The XRD diagram of GO in Fig. 1(a) finds the strong diffraction peak of GO appears at 12 degrees, which indicates that the oxide of graphite has been successfully synthesized.<sup>22</sup> It can be seen from Fig. 1(a) that the obvious diffraction peaks are observed at 30.0, 35.4, 43.4, 57.1 and 62.7 degrees respectively. According to the PDF card, namely PDF#03-0864, CoFe<sub>2</sub>O<sub>4</sub> has been successfully synthesized. Fig. 1(b) XRD patterns of CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts with different CoFe<sub>2</sub>O<sub>4</sub> loadings show that

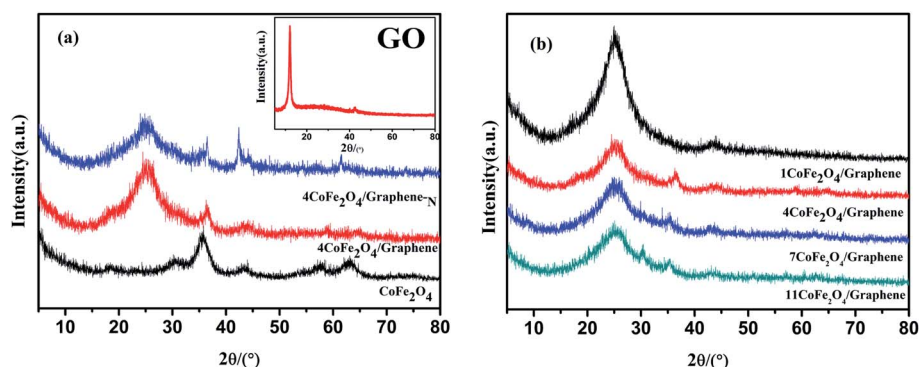


Fig. 1 XRD patterns of (a) GO, CoFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>/graphene, CoFe<sub>2</sub>O<sub>4</sub>/graphene-N, (b) CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts with different loadings.



there are obvious characteristic peaks of graphene at 25.2 degrees,<sup>23</sup> proving that graphene oxide has been successfully reduced during the preparation of the catalysts. At the same time, the diffraction peaks of  $\text{CoFe}_2\text{O}_4$  can be observed, indicating that  $\text{CoFe}_2\text{O}_4/\text{graphene}$  catalysts has been successfully synthesized.

Fig. 2 reveals  $\text{CoFe}_2\text{O}_4$  nanoparticles distribute on the surface of graphene. From the TEM diagram of  $\text{CoFe}_2\text{O}_4/\text{graphene}$ , it can be found that the active components are aggregated, and the distribution of  $\text{CoFe}_2\text{O}_4$  in  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalysts is more uniform. The results show that nitrogen doped was beneficial to the uniform distribution of the active components and to make a good contact with the reactants in  $\text{NH}_3\text{-SCR}$  test, thereby enhancing the reactivity of the catalysts.

Fig. 3 shows nitrogen adsorption–desorption isotherms of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ . It can be seen from the diagram that all types of catalytic isotherms are IV type and the lagging ring type is H1 type. The results show that the catalysts of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  contain typical mesoporous structures, and the isotherm hysteresis is related to the existence of voids.

Table 1 is the specific surface area, pore volume and pore size parameters of GO,  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalysts. It was found that the specific surface area of  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalysts was reduced, but its denitrification activity was higher than that of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  catalysts. This indicated that the denitrification activity of the catalysts was not only related to the specific surface area but also to the acidic site and redox performance of the catalysts.

### 3.2 Nitrogen-doped enhances the denitrification activity of $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ catalysts

Fig. 4 shows the  $\text{CoFe}_2\text{O}_4/\text{graphene}$  catalysts of different loadings and the denitrification activity of  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ . It can be seen from the graph that the denitrification activity of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  catalysts with different loading amount increases with the increase of the reaction temperature when it is less than 250 °C. When the reaction temperature is at 250 °C, the conversion of  $\text{NO}_x$  of all catalysts is above 95%, which indicates that the catalysts have good denitrification activity at low temperature. The SCR catalytic activity of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  catalyst increases and then decreases with the increasing of the loadings. Compared with  $\text{CoFe}_2\text{O}_4/\text{graphene}$  catalysts of 1%, 7% and 11% loading respectively,  $\text{CoFe}_2\text{O}_4/\text{graphene}$  catalysts with 4% loading have the highest denitrification conversion in the range of 200–400 °C, indicating that the optimum loading of the prepared  $\text{CoFe}_2\text{O}_4/\text{graphene}$  catalysts was 4%. Compared with  $4\text{CoFe}_2\text{O}_4/\text{graphene}$  catalysts,  $4\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalyst exhibits higher denitrification activity at low temperature in the range of 150–300 °C. It is due to the more uniform distribution of  $\text{CoFe}_2\text{O}_4$  after nitrogen doped. It is also related to the acidic site, redox performance of the catalysts and the synergetic effect between  $\text{CoFe}_2\text{O}_4$  and N-doped graphene support. The literature reported the synergetic effect can enhance photocatalytic activity and photostability.<sup>25,26</sup> Compared with the reported supported catalysts,  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalysts have better denitrification activity (Table 2).<sup>27–29</sup>

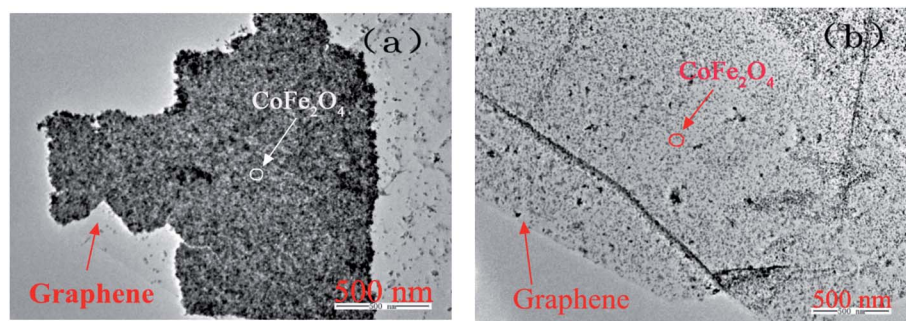


Fig. 2 TEM patterns of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  (a) and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  (b).

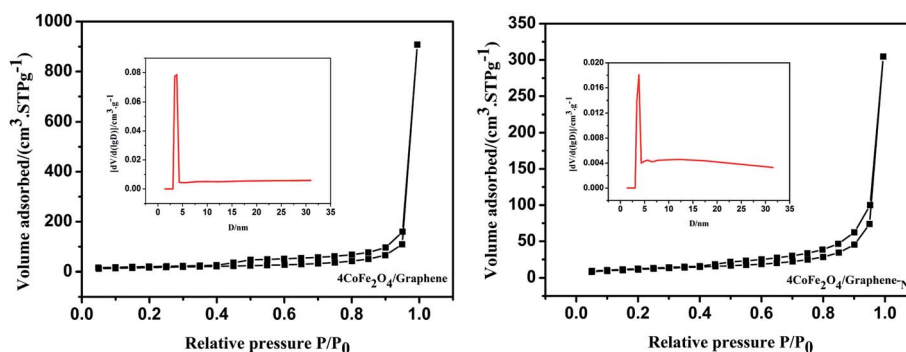
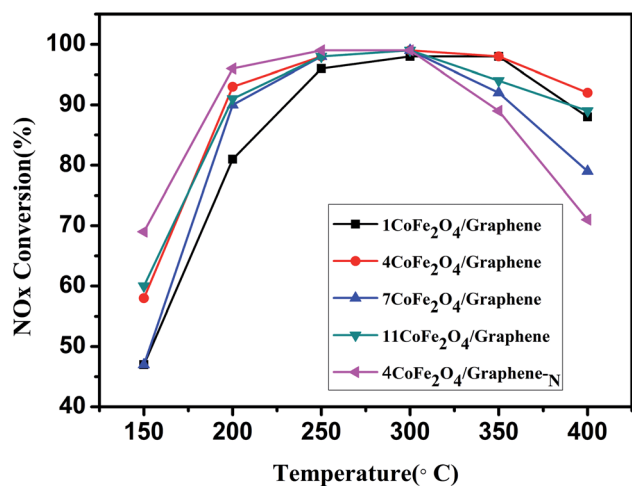


Fig. 3 Nitrogen adsorption–desorption isotherms of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ .



**Table 1** The specific surface area, pore volume and average pore size of GO, CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N

| Sample                                       | $S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> ) | $V_{\text{Total}}$ (cm <sup>3</sup> g <sup>-1</sup> ) | Average pore size (nm) |
|--|--|---|------------------------|
| GO <sup>24</sup>                             | 337  | 1.290   | 3.820                  |
| CoFe <sub>2</sub> O <sub>4</sub> /graphene   | 58   | 0.268   | 3.828                  |
| CoFe <sub>2</sub> O <sub>4</sub> /graphene-N | 40   | 0.158   | 3.825                  |



**Fig. 4** NH<sub>3</sub>-SCR activity of CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts with different loadings and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts. Reaction conditions: NH<sub>3</sub> (500 ppm), NO (500 ppm), O<sub>2</sub> 5%, N<sub>2</sub> as balanced gas, total gas flow (100 ml min<sup>-1</sup>).

### 3.3 Nitrogen-doped enhances the denitrification mechanism of CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts

Fig. 5(a) is a wide scan of XPS spectrum of CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N. The binding energy at 284.6 eV, 529.8 eV, 711.6 eV and 780.9 eV attributes to C 1s, O 1s, Fe 2p and Co 2p, respectively.<sup>30</sup> Fig. 5(b) is a C 1s XPS diagram of CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N. The peaks at 284.6 eV and 286.5 eV belong to the C=C and C-O functional groups of graphene, respectively.<sup>31</sup> The C-N bonds were also detected at 285.6 and 287.1 eV, which is attributed to sp<sup>2</sup> and sp<sup>3</sup> bonded C-N, respectively.<sup>32</sup> Fig. 5(c) is a Fe 2p XPS diagram of CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N. The Fe 2p spectrum shows two peaks at 711.1 eV and 725.1 eV, which can be assigned to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>, respectively, indicating the presence of Fe<sup>3+</sup>.<sup>33</sup> Fig. 5(d) is a Co 2p XPS diagram of CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N. The Co 2p spectrum shows two peaks at 781.0 eV and 786.6 eV, which can be attributed to Co 2p<sub>3/2</sub> and its satellite peak. Other peaks are observed at

796.6 eV and 802.8 eV corresponding to the Co 2p<sub>1/2</sub> and its satellite peak, indicating the presence of Co<sup>2+</sup>.<sup>34</sup> It indicates that CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts have been successfully synthesized, which is consistent with the XRD results. Fig. 5(e) is the N 1s XPS diagram of CoFe<sub>2</sub>O<sub>4</sub>/graphene-N. The peak at 398.8 eV belongs to pyridinic nitrogen; the peak at 399.8 eV belongs to pyrrolic nitrogen; and the peak at 401.6 eV belongs to graphitic nitrogen.<sup>35</sup> Table 3 exhibits the percentage of pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen for the CoFe<sub>2</sub>O<sub>4</sub>/graphene-N according to the XPS. The percentage of pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen for CoFe<sub>2</sub>O<sub>4</sub>/graphene-N is 42.42%, 35.89% and 21.69%, respectively. Among the three nitrogen species, pyridinic nitrogen is considered as the main active site for catalyzing oxygen reduction reaction, which can effectively improve the catalytic performance of CoFe<sub>2</sub>O<sub>4</sub>/graphene-N.<sup>36</sup> Fig. 5(f) is the O 1s XPS diagram of CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/g-N. The characteristic peaks of lattice oxygen (O<sub>β</sub>) at 530.4 eV, adsorb oxygen (O<sub>α</sub>) at 531.7 eV and surface oxygen (O<sub>γ</sub>) at 533.6 eV can be clearly seen from Fig. 5. It can be seen that the adsorbed oxygen (O<sub>α</sub>) ratio is calculated by O<sub>α</sub>/(O<sub>α</sub> + O<sub>β</sub>) for CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N. The calculated O<sub>α</sub> ratio (42.9%) of CoFe<sub>2</sub>O<sub>4</sub>/graphene is slightly higher than that (40.3%) of CoFe<sub>2</sub>O<sub>4</sub>/graphene-N. Surface adsorbed oxygen (O<sub>α</sub>) has higher mobility than lattice oxygen (O<sub>β</sub>) in SCR reaction,<sup>37</sup> which is helpful to improve the denitrification activity of catalysts, which is consistent with the test results of denitrification activity of catalysts. It means that the high denitrification activity of the CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts is related to other factors.

Fig. 6 is the NH<sub>3</sub>-TPD diagram of CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N. It can be seen that CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts have two desorption peaks. Comparing the two curves, CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts have higher peak temperature and peak area than CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts. This indicates that the acid strength and quantity of CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts are superior to that of CoFe<sub>2</sub>O<sub>4</sub>/graphene catalysts, and the increase of acid sites of catalysts promotes the denitrification activity of catalysts.<sup>38</sup>

Fig. 7 is the H<sub>2</sub>-TPR diagram of CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts. As is shown, the reduction peaks of CoFe<sub>2</sub>O<sub>4</sub>/graphene and CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts occur at 462 °C and 388 °C respectively. Compared with CoFe<sub>2</sub>O<sub>4</sub>/graphene, the peak of CoFe<sub>2</sub>O<sub>4</sub>/graphene-N moved to low temperature, indicating that the catalysts have better reduction performance at low temperature. In addition, the reduction peak area of CoFe<sub>2</sub>O<sub>4</sub>/graphene-N catalysts increases, indicating that the redox performance of the catalysts increases, thus increasing the denitrification activity of the catalysts.<sup>39</sup>

**Table 2** The catalytic activities of the reported denitrification catalysts

| Catalysts  | NO <sub>x</sub> conversion (temperature range) | GHSV                   | References |
|--|--|------------------------|------------|
| Cu-ZSM-5   | ≥80% (250–350 °C)                              | 80 000 h <sup>-1</sup> | 27         |
| CeO <sub>2</sub> -ZrO <sub>2</sub> /TiO <sub>2</sub> | ≥80% (250–350 °C)                              | 71 400 h <sup>-1</sup> | 28         |
| CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>     | ≥90% (300–400 °C)                              | 7200 h <sup>-1</sup>   | 29         |



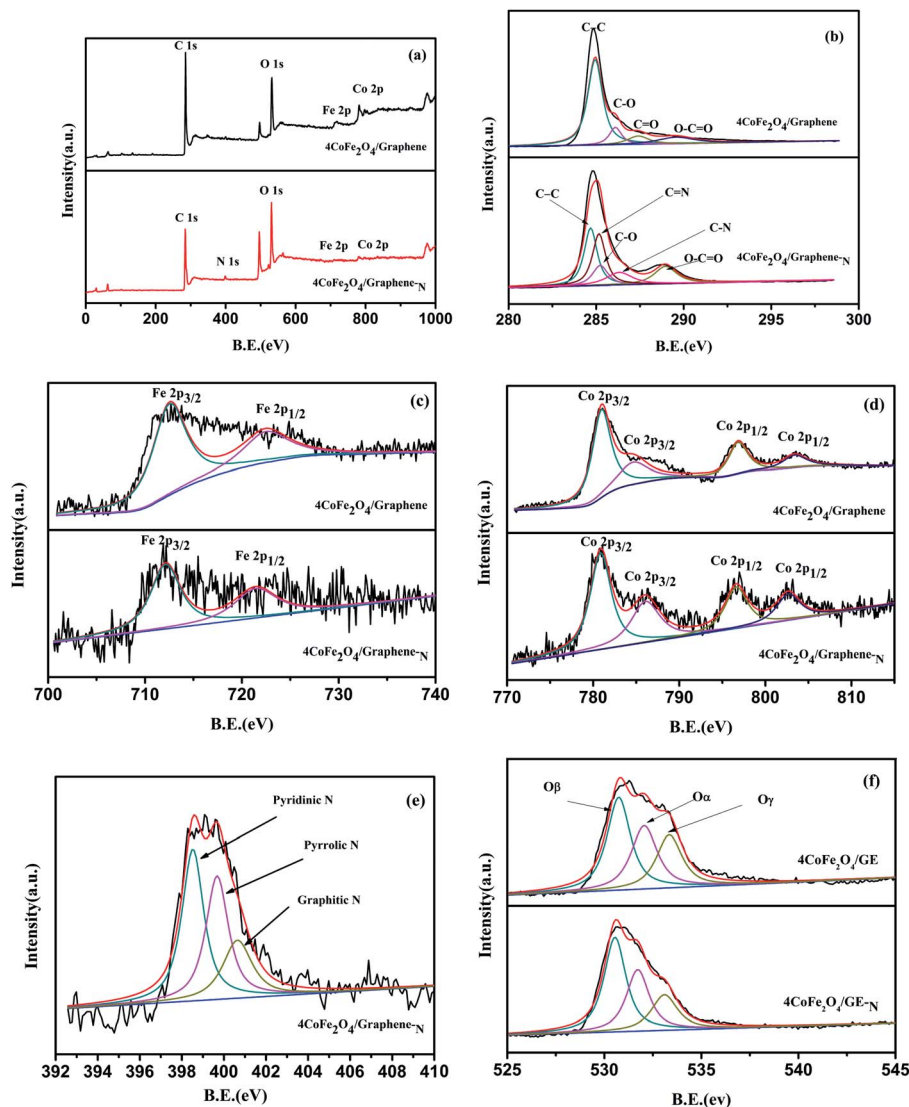


Fig. 5 (a) XPS spectra of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  (b) C 1s XPS spectra of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  (c) Fe 2p XPS spectra of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  (d) Co 2p XPS spectra of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  (e) N 1s XPS spectra of  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  (f) O 1s XPS spectra of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ .

### 3.4 Test of water and sulfur resistance of $\text{CoFe}_2\text{O}_4/\text{graphene}$ and $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ catalysts

Fig. 8 is a test of water and sulfur resistance of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalysts. It is obvious that the denitrification activity of  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  is higher than that of  $\text{CoFe}_2\text{O}_4/\text{graphene}$ , indicating that nitrogen doped is beneficial to improving the water and sulfur resistance of the catalysts. The denitrification activity of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalysts is tested in the presence of  $\text{SO}_2$ . The denitrification conversion rate of  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$

catalysts is relatively poor when the reaction temperature is below  $250^\circ\text{C}$ . The reason was that  $\text{SO}_2$  reacts with  $\text{NH}_3$  to form sulfate that covers the active sites of the catalysts and blocks the channels of the catalysts, which weakens the catalytic activity. At the high temperature,  $\text{SO}_2$  on the surface of the catalysts is converted to  $\text{SO}_4^{2-}$ , resulting in the increase of surface acidity of the catalysts and the enhancement of the denitrification activity of the catalysts.<sup>40</sup> The poor water resistance of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalysts is attributed to the competitive adsorption of  $\text{H}_2\text{O}$  and reactive gases ( $\text{NH}_3$ ,  $\text{O}_2$ ,  $\text{NO}$ )

Table 3 Percentage of pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen of  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  from the XPS

| Catalysts                                   | Pyridinic nitrogen/% | Pyrrolic nitrogen/% | Graphitic nitrogen/% |
|---|----------------------|---------------------|----------------------|
| $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ | 42.42%               | 35.89%              | 21.69%               |



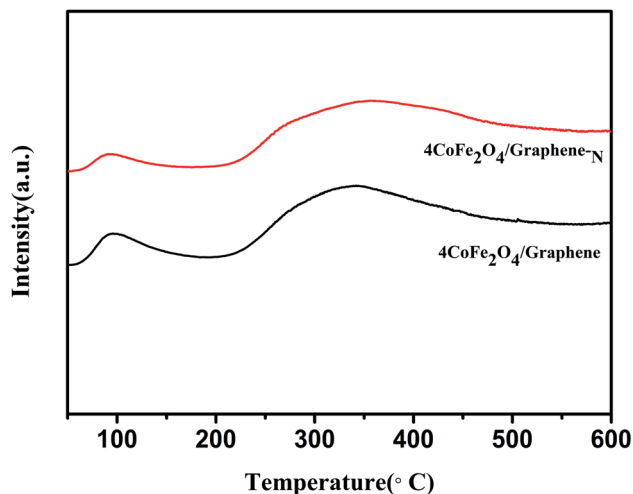


Fig. 6  $\text{NH}_3$ -TPD diagram of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ .

on the surface of the catalysts, and the hydroxyl groups generated by the adsorbed water on the surface of the catalysts neutralize the acidic sites on the surface of the catalysts, resulting in the deterioration of the denitrification activity of the catalysts.<sup>41</sup>

### 3.5 Repeatability test of $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ catalyst

Fig. 9 shows the repeatability of  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalyst for four times. It can be seen from the Fig. 9 that the denitrification activity of the reused  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  (four times) significantly decreased under 250 °C compared with the fresh catalyst. However, it is interesting that the activity of the reused catalyst can basically maintain invariable in the temperature of 250–300 °C. In addition, the reused  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  do not significantly decrease the conversion of  $\text{NO}_x$  in the range of temperature from 300 °C to 400 °C.

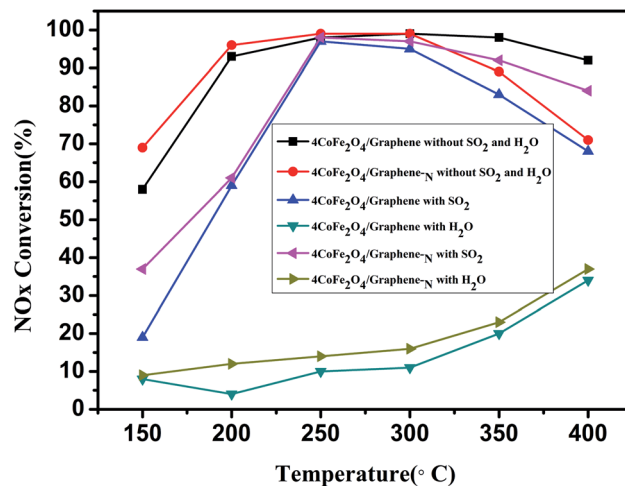


Fig. 8 The effect of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  on  $\text{NO}_x$  conversion over  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ . Reaction conditions:  $\text{NH}_3$  (500 ppm),  $\text{NO}$  (500 ppm),  $\text{O}_2$  5%,  $\text{SO}_2$  (100 ppm),  $\text{H}_2\text{O}$  3%,  $\text{N}_2$  as balanced gas, total gas flow (100  $\text{ml min}^{-1}$ ).

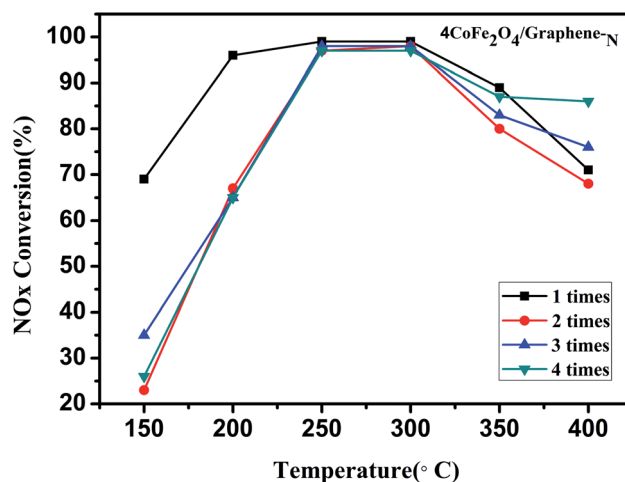


Fig. 9 Repeatability of  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalyst.

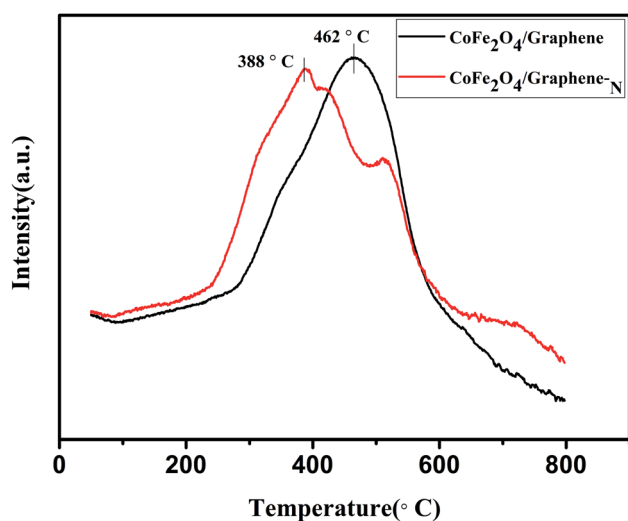


Fig. 7  $\text{H}_2$ -TPR diagram of  $\text{CoFe}_2\text{O}_4/\text{graphene}$  and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$ .

## 4. Conclusions

$\text{CoFe}_2\text{O}_4/\text{graphene}$  catalysts and  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  catalysts were prepared. When the loading amount is 4%, the denitrification activity of the catalysts is the best, and the conversion rate of  $\text{NO}_x$  reaches 99% at 250–300 °C. TEM showed that nitrogen doped made the distribution of the active components more uniform on the carrier.  $\text{NH}_3$ -TPD and  $\text{H}_2$ -TPR showed that nitrogen doped resulted in more acidic sites on the surface of the catalysts and improved the redox performance of the catalysts.  $\text{CoFe}_2\text{O}_4/\text{graphene-N}$  has better denitrification activity at low temperature than  $\text{CoFe}_2\text{O}_4/\text{graphene}$ , and the conversion rate of  $\text{NO}_x$  reaches more than 95% at 200–300 °C.

## Conflicts of interest

There are no conflicts to declare.



## Acknowledgements

This article was supported by National Natural Science Foundation of China (51708309), Heilongjiang Provincial Natural Science Foundation (QC2017065), The Fundamental Research Funds in Heilongjiang Provincial Universities (No. 135109103), Specialized Subject of Plant Food Processing Technology of Heilongjiang Education Department (YSTSXX201872), Qiqihar University Graduate Student Innovative Research Projects (YJSCX2018-032X).

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