Low-temperature (NO + O₂) adsorption performance of alkaline earth metal-doped C-FDU-15

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A B S T R A C T

To improve the removal capacity of NO + O₂ effectively, the alkaline earth metal-doped order mesoporous carbon (A-C-FDU-15(0.001) (A = Mg, Ca, Sr and Ba)) and Mg-C-FDU-15(x) (x = 0.001–0.003) samples were prepared, and their physicochemical and NO + O₂ adsorption properties were determined by means of various techniques. The results show that the sequence in (NO + O₂) adsorption performance was as follows: Mg-C-FDU-15(0.001) (93.2 mg/g) > Ca-C-FDU-15(0.001) (82.2 mg/g) > Sr-C-FDU-15(0.001) (76.1 mg/g) > Ba-C-FDU-15(0.001) (72.9 mg/g) > C-FDU-15 (67.1 mg/g). Among all of the A-C-FDU-15(0.001) samples, Mg-C-FDU-15(0.001) possessed the highest (NO + O₂) adsorption capacity (106.2 mg/g). The species of alkaline earth metals and basic sites were important factors determining the adsorption of NO + O₂ on the A-C-FDU-15(x) samples, and (NO + O₂) adsorption on the samples was mainly chemical adsorption. Combined with the results of (NO + O₂)-temperature-programmed desorption (NO + O₂)-TPD and in situ diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization, we deduced that there were two main pathways for (NO + O₂) adsorption: one was the conversion of NO and O₂ to NO₂ and then part of NO₂ was converted to NO₃⁻ and NO₃⁻; and the other was the direct oxidation of NO to NO₃⁻ and NO₃⁻.

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I N T R O D U C T I O N

Nitrogen oxides (NOₓ) are one of atmospheric pollutants. The NOₓ is mainly emitted from burning coals and motor vehicle exhaust (Chang et al., 2013; You et al., 2017). The hazard of NOₓ is widespread, which includes several aspects: (i) it can constitute air pollution and produces photochemical smog; (ii) it is not only one of the main sources of acid rain, but also a carcinogen; (iii) hydrocarbon compounds and NOₓ can easily generate secondary toxic pollutants under the irradiation of strong light; and (iv) it can also damage the ozone layer.

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The environment will be greatly affected by acid rain, ozone layer destruction, greenhouse effect, and other adverse consequences caused by NOx emissions. As the increase of NOx emissions, the pollution induced by NOx is increasingly concerned.

At present, the matured NO control technologies are the selective catalytic reduction (SCR) and NOx storage/reduction (NSR), which are successfully used to reduce NOx emissions of diesel engine (Han et al., 2019; Guo et al., 2015). However, the two technologies can only be used under the conditions of high concentrations and high temperatures, which restrict their wide applications. In the closed and semi-closed space (e.g., industrial workshops and highway tunnels), it is difficult to effectively remove NOx over the common denitration materials due to the fact that NOx exists under the low temperature and low concentration conditions (Pan et al., 2017). Activated carbon (AC) is the most commonly used carbon material in adsorption. The AC can adsorb NOx in low-concentration exhaust gas, and such an adsorption can also be recycled, which is more suitable than the other methods (Abdulrasheed et al., 2018; Fu et al., 2017). However, its adsorption performance needs to be further improved. Thus, it is highly desired to develop high-performance adsorption materials. Ordered mesoporous carbon (C-FDU-15) has been shown to be an excellent NOx adsorbent due to its unique properties (e.g., easy mass transfer and rich internal surface) (Yu et al., 2017).

NO cannot be removed by adsorption alone, relying on its stability at low concentrations. Some researchers found that NO was easier to remove when it is oxidized to NO2 (Hu et al., 2019; Li et al., 2019a). Since NO2 is an acid gas and alkaline earth metals can promote the adsorption of acid gas, combination of alkaline earth metals and C-FDU-15 is expected to obtain materials with high NO adsorption performance (Svensson et al., 2019; Song et al., 2019; Uematsu et al., 2019). However, few studies on the adsorption of NO on the alkaline earth metals-doped C-FDU-15 adsorbents at low temperatures have been seen in the literature.

In this work, the alkaline earth metals (A = Mg, Ca, Sr and Ba)-doped C-FDU-15 (A-C-FDU-15) samples with the molar ratio of alkaline earth metal to C-FDU-15 of 0.001:1 were prepared by the in situ method, and their structures and NO adsorption performance were determined. At the same time, the optimal doped alkaline earth metal and its doped amount were investigated to obtain a new and effective low-temperature NO removal material.

1. Materials and methods

1.1. Chemicals

Polyethylene oxide–polypropylene oxide–polyethylene (Pluronic 127, Acros), phenol (Acros), formaldehyde (Acros), magnesium nitrate hexahydrate (Mg(NO3)2·6H2O, Aladdin), calcium nitrate tetrahydrate (Ca(NO3)2·4H2O, Aladdin), barium nitrate (Ba(NO3)2, Aladdin), and strontium nitrate (Sr(NO3)2, Aladdin). The other chemicals were purchased from Shanghai Chemical Corp.

1.2. Preparation of resol

After 7.37 g of formaldehyde (37 wt.%) and 4.7 g of phenol were mixed at 40°C, a NaOH aqueous solution (20 wt.%) was added to the mixture, then the temperature was increased to 70°C and the mixed solution was stirred at 70°C for 1 hr. The pH value of the solution was tuned to 7 with a HCl aqueous solution (3.0 mol/L) after being cooled to room temperature. The water in the mixture was evaporated in a vacuum oven, and the left NaCl was removed by centrifugation (2300 r/min). Ethanol (66.9 mL) was added to prepare a resin solution of 20 wt.%. 

1.3. Preparation of A-C-FDU-15(x)

In a typical synthesis, the alkaline earth metal (A = Ca, Mg, Ba or Sr) and 5.0 g of F127 were added in 120.0 mL of ethanol and 5 mL of HCl aqueous solution (0.1 mol/L), then 25 mL of resol was added using the separating funnel and stirred for 10 min. The solution was transferred to some dishes at 30°C for 3 hr to produce a resol membrane, which was heated in an oven at 110°C for 15 hr. The sample was roasted at a heating rate of 1°C/min from room temperature to 600°C and kept at 600°C for 2 hr under N2 atmosphere, followed by calcining from 600 to 900°C and maintained at 900°C for 2 hr under N2 atmosphere. The obtained samples were called as A-C-FDU-15(x) (A = Ca, Mg, Ba, and Sr), where x was the molar ratio of alkaline earth metal/C-FDU-15.

1.4. Characterization

The simulated mixed gas is often used in the NOx treatment experiments. Chen et al. (2014) used the (500 ppmV NO + 5 vol.% O2 + N2 (balance)) mixed gas for NO adsorption on the ordered mesoporous carbon (OMC) and cerium-containing OMC (Ce-OMC). Li et al. (2017) studied the SCR reaction over the CrO3/sargassum-based activated carbon in the presence of the (500 ppmV NO + 5 vol.% O2 + N2 (balance)) mixed gas. Hence, the (500 ppmV NO + 5 vol.% O2 + N2 (balance)) mixed gas was also used in our present work. The thermogravimetric adsorption was measured by thermogravimetric analyzer (NETZSCH-STA-449-F5, NETZSCH, Germany) and the samples were saturated with 500 ppmV NO and 5 vol.% O3 with N2 as balance. The samples were regenerated after five recycles. The deactivated samples were first washed with a hydrochloric acid solution (1.0 mol/L) and deionized water several times. Then, the samples were dried in an oven at 120°C overnight. Before the regeneration efficiency (RE (%)) was evaluated, the samples were heated in a N2 flow of 50 mL/min at 400°C for 1 hr.

The effect of water on (NO + O2) adsorption was examined on the apparatus (BJBUILDER-PCA-1200, BJBUILDER, China). The mixed gas (500 ppmV NO + 5 vol.% O2 + 5 vol.% H2O + N2 (balance)) was first adsorbed on the 400°C-pretreated Mg-C-FDU-15(0.003) sample for 5 hr, then the sample was purged with He for 0.5 hr, and finally heated to 400°C for carrying out the temperature-programmed desorption (TPD) experiment. The structure of A-C-FDU-15(x) samples was characterized by X-ray diffraction (XRD) (X’Pert Pro-MPD-Advance powder diffractometer, Panalytical, Netherland) with a secondary
beam graphite monochromator using nickel-filtered Cu Kα radiation. Nitrogen adsorption experiments at −196°C were carried out on a Brunner–Emmet–Teller (BET) instrument (JW-BK132F, JWGB SCI & TECH, China). The total pore volume was obtained from the N₂ adsorption branches using t-plot method, and the Barret–Joyner–Halenda (BJH) method was used to calculate the mesopore sizes. In addition, transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) were used to determine the pore structures and element compositions of the samples at 120 kV on an instrument (JEM-2100F, NIPPON SODA, Japan). Oxygen temperature-programmed desorption (O₂–TPD), CO₂ temperature-programmed desorption of (CO₂–TPD), and (NO + O₂) temperature-programmed desorption ((NO + O₂)–TPD) were conducted on a apparatus (BJBUILDER-PCA-1200, BJBUILDER, China) to measure the amounts of O₂ desorption, basic sites, and NO₂ desorption, respectively. The 500 ppmV NO + 5 vol.% O₂ and N₂ were used when the characterization of the samples was made. The samples were heated from room temperature to 400°C at a heating rate of 10°C/min and kept in a He flow of 30 mL/min at 400°C for 1 hr. The in situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was used to record the spectra of the samples per 30 min with an average of 10 scans on a spectrometer (TENSOR II, Bruker Vertex 80, Germany). In the NO oxidation experiment, 100 mg of the typical sample was pretreated at 400°C in a N₂ flow of 100 mL/min for 1 hr, then cooled to room temperature, and finally the (NO + O₂) was adsorbed for 6 hr to reach the adsorption–desorption equilibrium on the sample. After that, the NO conversions were measured at an interval of 50°C from 25 to 200°C on the NO–NO₂–NOₓ analyzer high level apparatus (Model 42i-HL, Thermo, USA).

2. Results and discussion

2.1. Adsorbents characterization

2.1.1. Adsorption performance

Generally speaking, N₂ hardly influences the results of adsorption on the carbon materials. Some researchers studied the selective adsorption of CO₂ and N₂, and proved that adsorption of N₂ on the carbon materials at room temperature could be almost ignored. For example, Yu et al. (2020) observed that N₂ adsorption capacities were quite low (5.52–9.36 mg/g at 25°C and 1 atm) on the electrospun carbon nanofibers. Li et al. (2019b) studied the selectivity adsorption performance of CO₂/N₂ on biomass-derived porous carbon, and found that N₂ was hardly adsorbed. After investigating the CO₂/N₂ selectivity on nitrogen-doped porous carbons, Wang et al. (2018) claimed that N₂ adsorption could be ignored. Moreover, according to the results of the (NO + O₂)–TPD and DRIFTS experiments (shown in the later sections), we concluded that N₂ exerted no significant impact on the adsorption results. Therefore, the influence of N₂ on (NO + O₂) adsorption could be ignored.

Fig. 1 shows (NO + O₂) adsorption performance of the A-C-FDU-15(0.001) (A = Ca, Mg, Ba and Sr) samples. The mixture gas (500 ppmV NO + 5 vol.% O₂ + N₂ (balance)) was adsorbed on each sample at 30°C for 5 hr, and the adsorption performance is presented in Table 1. The adsorption capacity decreased in the order of Mg-C-FDU-15(0.001) (93.2 mg/g) > Ca-C-FDU-15(0.001) (82.2 mg/g) > Sr-C-FDU-15(0.001) (76.1 mg/g) > Ba-C-FDU-15(0.001) (72.9 mg/g) > C-FDU-15 (76.2 mg/g). Obviously, the (NO + O₂) adsorption capacity of A-C-FDU-15(0.001) was larger than that of C-FDU-15. Among all of the A-C-FDU-15(0.001) samples, Mg-C-FDU-15(0.001) possessed the largest adsorption capacity, indicating that the (NO + O₂) adsorption capacity was determined by the nature of the alkaline earth metal.

It is necessary to compare the (NO + O₂) adsorption performance of C-FDU-15 with that of the commercial activated carbon (AC). Obviously, (NO + O₂) adsorption capacity (71.7 mg/g) of C-FDU-15 was much larger than that (25.3 mg/g) of AC (Wu et al., 2020). Moreover, (NO + O₂) adsorption capacities of the alkali metal-modified C-FDU-15 samples were larger than those of the AC and alkali metal-doped AC samples. For example, Ghouma et al. (2018) found that the optimal (NO + O₂) adsorption capacity of the alkali metal-modified activated carbon derived from the physical activation of olive stones was ca. 66.96 mg/g.

2.1.2. Texture characterization

Wide-angle (2θ = 10–60°) XRD patterns of the A-C-FDU-15(0.001) and C-FDU-15 samples are shown in Fig. S1a. It was observed that the diffraction peaks at 2θ = 26° and 44° were characteristics of the carbon materials (Zhao et al., 2016), indicating that alkaline earth metals did not affect carbonation of the A-C-FDU-15(0.001) samples. In addition, there were no other peaks, suggesting that the alkaline earth metals existed in high dispersion of C-FDU-15 (Zhang et al., 2019). Fig. S1b shows the low-angle (2θ = 0.5 – 5°) XRD patterns of the A-C-FDU-15(0.001) and C-FDU-15 samples. There was one diffraction peak at 2θ = 0.9°, attributable to the (100) crystal plane of the ordered mesopores. That is to say, the samples possessed a well-ordered mesoporous structure (Wang et al., 2019; Shou et al., 2016).
Shown in Fig. 2a are the N₂ adsorption–desorption isotherms of the samples. The C-FDU-15 was a mesoporous material with a typical type-IV isotherm, while the A-C-FDU-15(0.001) samples were not the same as the C-FDU-15 sample. N₂ adsorption–desorption isotherms of the A-C-FDU-15(0.001) samples exhibited a steep slope in the high p/p₀ range, which was characteristics of micropores. This result might be due to the fact that the carbon channels were partially blocked (Chen et al., 2019).

The textural parameters of the samples are listed in Table 2. The specific surface areas and pore volumes decreased in the sequence of C-FDU-15 (420 m²/g, 0.28 cm³/g) > Ba-C-FDU-15(0.001) (407 m²/g, 0.24 cm³/g) > Mg-C-FDU-15(0.001) (403 m²/g, 0.24 cm³/g) > Ca-C-FDU-15(0.001) (401 m²/g, 0.23 cm³/g) > Sr-C-FDU-15(0.001) (389 m²/g, 0.22 cm³/g). Surface areas and pore volumes of the A-C-FDU-15(0.001) samples were close, and decreased only slightly as compared with those of C-FDU-15. The pore sizes of C-FDU-15, Mg-C-FDU-15(0.001), Ca-C-FDU-15(0.001), Sr-C-FDU-15(0.001) and Ba-C-FDU-15(0.001) were 2.68, 2.79, 2.74, 2.92 and 3.01 nm, respectively. Textural properties of the A-C-FDU-15(0.001) samples were not consistent with their (NO + O₂) adsorption performance, indicating that the textural properties of A-C-FDU-15(0.001) do not show a significant effect on the (NO + O₂) adsorption performance (Fig. 2c).

### 2.1.3. Basic sites in the samples

CO₂–TPD was performed to determine basic sites of the samples. Each profile in Fig. 3a shows three peaks: low-temperature peak (LTP), medium-temperature peak (MTP), and high-temperature peak (HTP), which corresponded to three types of the basic species: the LTP at 30–200°C was assigned to bicarbonate, where CO₂ molecules were weakly adsorbed at the surface hydroxyl groups; the MTP at 220–290°C was ascribed to bidentate hydroxyl, which was due to the oxygen in the alkaline earth metal oxide and O₂⁻ pairs; and the HTP at 380–420°C was attributed to unidentified carbonate, due to the presence of free low-coordinate oxide ions (Guo et al., 2020a, 2020b). After quantitative analysis via the curve-fitting, CO₂ desorption amounts (total amounts of basic sites) of the samples are listed in Table 3. Apparently, CO₂ desorption amount decreased in the order of Mg-C-FDU-15(0.001) (246.9 mg/g) > Ca-C-FDU-15(0.001) (198.3 mg/g) > Ba-C-FDU-15(0.001) (64.6 mg/g) > Sr-C-FDU-15(0.001) (59.8 mg/g) > C-FDU-15 (9.0 mg/g), in which CO₂ desorption amounts of the A-C-FDU-15(0.001) samples were significantly higher than that of the C-FDU-15 sample. Therefore, doping of the alkaline earth elements could improve alkalinity of the C-FDU-15 sample. The (NO + O₂) adsorption capacities (Fig. 3b) were consistent with alkalinity of the samples. In other words, doping of the alkaline earth metal was the decisive factor influencing the (NO + O₂) adsorption performance.

### 2.1.4. Oxygen vacancies

Fig. S2a presents oxygen-releasing properties of the A-C-FDU-15(0.001) and C-FDU-15 samples, as revealed in their O₂–TPD profiles. The O₂ desorption from C-FDU-15 was tiny, i.e., only small amounts of O₂ desorption at 200 and 400°C. The A-C-FDU-15(0.001) samples exhibited similar O₂ desorption profiles, which clearly showed two distinct desorption peaks with the maximum intensity at around 260 and 400°C, implying that there were similar oxygen vacancies in the A-C-FDU-15(0.001) samples. The desorbed oxygen amounts are listed in Table 3. The amount of O₂ desorption decreased as

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**Table 1 – (NO + O₂) adsorption performance of the A-C-FDU-15(0.001) and Mg-C-FDU-15(x) samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total adsorption amount (mg/g)</th>
<th>Amount of chemical adsorption (mg/g)</th>
<th>Amount of physical adsorption (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-FDU-15</td>
<td>67.1</td>
<td>66.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.001)</td>
<td>93.2</td>
<td>88.3</td>
<td>4.9</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.002)</td>
<td>106.2</td>
<td>103.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.003)</td>
<td>102.2</td>
<td>100.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Ca-C-FDU-15(0.001)</td>
<td>82.2</td>
<td>80.3</td>
<td>1.9</td>
</tr>
<tr>
<td>Sr-C-FDU-15(0.001)</td>
<td>76.1</td>
<td>75.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Ba-C-FDU-15(0.001)</td>
<td>72.9</td>
<td>72.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

---

**Table 2 – Textural parameters of the A-C-FDU-15(0.001) and Mg-C-FDU-15(x) samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET¹ surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-FDU-15</td>
<td>420</td>
<td>0.28</td>
<td>2.68</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.001)</td>
<td>403</td>
<td>0.24</td>
<td>2.74</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.002)</td>
<td>395</td>
<td>0.26</td>
<td>2.62</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.003)</td>
<td>318</td>
<td>0.26</td>
<td>3.23</td>
</tr>
<tr>
<td>Ca-C-FDU-15(0.001)</td>
<td>401</td>
<td>0.23</td>
<td>2.92</td>
</tr>
<tr>
<td>Sr-C-FDU-15(0.001)</td>
<td>389</td>
<td>0.22</td>
<td>3.01</td>
</tr>
<tr>
<td>Ba-C-FDU-15(0.001)</td>
<td>407</td>
<td>0.24</td>
<td>2.79</td>
</tr>
</tbody>
</table>

¹ BET: Brunner–Emmet–Teller.
2.1.6. Obviously, Ca-C-FDU-15(0.001) was the sample that could release the most NO+O2 isotherms and adsorption performance (Fig. S2b). This result demonstrated that the oxygen vacancy was not the key factor influencing the adsorption performance. At the same time, the NO adsorption amounts on the A-C-FDU-15(0.001) and C-FDU-15 samples were much less than the NO+O2 adsorption amounts, indicating that the main role of the adsorbed O2 species was to oxidize NO during the adsorption process (Oyarzun et al., 2016).

### Table 3 – NOx, O2, and CO2 desorption from the A-C-FDU-15(0.001) and Mg-C-FDU-15(x) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Desorption of NOx</th>
<th>Desorption of O2</th>
<th>Desorption of CO2</th>
<th>Percentage of NO and O2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LT* peak (mg/g)</td>
<td>MT* peak (mg/g)</td>
<td>HT* peak (mg/g)</td>
<td>Total (mg/g)</td>
</tr>
<tr>
<td>C-FDU-15</td>
<td>31.9</td>
<td>14.7</td>
<td>6.3</td>
<td>53.0</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.001)</td>
<td>50.9</td>
<td>9.9</td>
<td>7.9</td>
<td>68.7</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.002)</td>
<td>56.8</td>
<td>14.2</td>
<td>1.1</td>
<td>72.1</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.003)</td>
<td>45.2</td>
<td>13.8</td>
<td>3.6</td>
<td>62.6</td>
</tr>
<tr>
<td>Ca-C-FDU-15(0.001)</td>
<td>48.7</td>
<td>9.6</td>
<td>7.4</td>
<td>65.8</td>
</tr>
<tr>
<td>Sr-C-FDU-15(0.001)</td>
<td>47.5</td>
<td>5.0</td>
<td>9.1</td>
<td>61.3</td>
</tr>
<tr>
<td>Ba-C-FDU-15(0.001)</td>
<td>41.8</td>
<td>12.9</td>
<td>3.8</td>
<td>58.5</td>
</tr>
</tbody>
</table>

*LT: low-temperature; MT: medium-temperature; HT: high-temperature.

follows: Ba-C-FDU-15(0.001) (8.81 mg/g) > Sr-C-FDU-15(0.001) (8.29 mg/g) > C-FDU-15 (2.61 mg/g) > Ca-C-FDU-15(0.001) (1.52 mg/g) = Mg-C-FDU-15(0.001) (1.40 mg/g). The sequence in O2 desorption amount of A-C-FDU-15(0.001) was not consistent with their (NO + O2) adsorption performance (Fig. S2b). The result demonstrated that the oxygen vacancy was not the key factor influencing the adsorption performance. At the same time, the NO adsorption amounts on the A-C-FDU-15(0.001) and C-FDU-15 samples were much less than the NO+O2 adsorption amounts, indicating that the main role of the adsorbed O2 species was to oxidize NO during the adsorption process (Oyarzun et al., 2016).

2.1.5. (NO + O2)-TPD of A-C-FDU-15(0.001)

Fig. 4 illustrates (NO + O2)-TPD profiles of the A-C-FDU-15(0.001) samples. The release of NOx was observed in the range of 30–550°C. Three regions of the NOx desorption profile of each A-C-FDU-15(0.001) sample were present: a strong low-temperature (LT) peak at 30–150°C, a medium-temperature (MT) peak at 150–270°C and a high-temperature (HT) peak at 400–420°C. The LT peak was assigned to NOx; the HT peak was ascribed to nitrites; and the MT peak was attributed to nitrites (Muckenhuber and Grothe, 2006; Sousa et al., 2013; Ghouma et al., 2015). Desorption amounts of NOx from the A-C-FDU-15(0.001) and C-FDU-15 samples were calculated and showed in Fig. S3 and Table 3. The sequence in NOx desorption amount was as follows: Mg-C-FDU-15(0.001) (68.7 mg/g) > Ca-C-FDU-15(0.001) (65.8 mg/g) > Sr-FDU-15(0.001) (61.3 mg/g) > Ba-C-FDU-15(0.001) (58.5 mg/g) > C-FDU-15 (53.0 mg/g). Obviously, NOx desorption amounts of the samples doped with various alkaline earth metals were different, and Mg-C-FDU-15(0.001) possessed the optimum adsorption performance. In addition, the NOx desorption amounts from A-C-FDU-15(0.001) (Fig. 4) were consistent with the (NO + O2) adsorption performance.

2.1.6. DRIFTS of (NO + O2) adsorption on A-C-FDU-15(0.001)

To investigate formation of nitro compounds on the A-C-FDU-15(0.001) and C-FDU-15 samples, the in situ DRIFTS experiments could provide necessary information on the (NO + O2) adsorption mechanisms. The DRIFTS spectra of (NO + O2) adsorption on the Ca-C-FDU-15(0.001) sample are shown in Fig. 5, and those of the A-C-FDU-15(0.001) samples are shown in Fig. S4. During the adsorption process of (NO + O2) on all of the samples, we detected five absorption bands at 833, 1356, 1390, 1415, and 1434 cm⁻¹ (López et al., 2016; Nguyen et al., 2018; Valle et al., 2018; Ji et al., 2015; Kim et al., 2012). The band at 833 cm⁻¹ was ascribed to the chemisorbed nitrite, the one at 1356 cm⁻¹ was assigned to the adsorbed nitrates formed via the interaction of NO and superoxide radicals, the one at 1390 cm⁻¹ was attributed to the free nitrate, the one at 1415 cm⁻¹ was characteristic of linear nitrite, and the weak peak at 1454 cm⁻¹ was due to the presence of nitro compounds in nitrite species. DRIFTS features characteristics of the nitrite (833, 1415, and 1434 cm⁻¹) and nitrates (1356 and 1390 cm⁻¹) of A-C-FDU-15(0.001) appeared simultaneously. When the bands of nitrates became steady, the ones of nitrates increased in intensity with time. After 5 hr of adsorption, intensity of nitrates increased no longer. After purging with N2 for 30 min, intensity of the bands did not change, demonstrating that most of the NO3 species were stable. Moreover, intensity of the bands of the A-C-FDU-15(0.001) samples (Fig. S4b-e) was stronger than that of the C-FDU-15 sample (Fig. S4a), indicating that (NO + O2) adsorption performance of the former was better than that of the latter. This result was consistent with the results of (NO + O2) adsorption experiments and (NO + O2)-TPD characterization (Figs. 1 and 4).

It should be noted that Pd can play an important role in promoting the oxidation of adsorbed nitrite to nitrate and providing additional NO adsorption sites in the samples. We have prepared the Pd/C-FDU-15(0.0005) sample (Pd/C molar ratio = 0.0005:1) and conducted the (NO + O2)-TPD experiment. By comparing the position and intensity of the desorption peaks of Pd/C-FDU-15(0.0005) and Mg-C-FDU-15(0.002) (Fig. 5), we can realize that Pd/C-FDU-15(0.0005) exhibited a stronger NO adsorption than Mg-C-FDU-15(0.002), and more amounts of the adsorbed nitrate and nitrite species were produced in the Pd/C-FDU-15(0.0005) sample. Ryu et al. (2018) and Ji et al. (2020) pointed out that the Pd in the samples provided the additional NO adsorption sites and promoted the oxidation of the adsorbed nitrite to nitrate. In addition, Onrubia-Calvo et al. (2020) and Theis (2016) investigated the effect of Pd on the NOx trap behavior, and observed that Pd could enhance the NOx trap. Hence, it would be benefi-
cial to load a noble metal in a catalyst for (NO + O₂) adsorption at low and medium temperatures.

2.2. Characterization of Mg-C-FDU-15(x)

Since Mg-C-FDU-15 exhibited the best (NO + O₂) adsorption performance of among the A-C-FDU-15 samples, we investigated the effect of (NO + O₂) adsorption on the Mg-C-FDU-15(x) (x = 0.001, 0.002, and 0.003) samples.
carbon-based samples is insignificant. Fig. S6 shows the NO\textsubscript{x} desorption from the Mg-C-FDU-15(0.003) sample in the range of 30–500°C. The overall desorbed amounts of NO\textsubscript{x} were similar in the presence and absence of water in the mixed gasses, which indicates that H\textsubscript{2}O did not influence NO adsorption on the Mg-C-FDU-15(0.003) sample surface. As pointed out by Yang et al. (2015), water could decrease NO\textsubscript{x} conversion due to the hindering effect of competitive adsorption between water and NH\textsubscript{3}, but not due to the prohibitive effect on NO adsorption. After investigating the impact of H\textsubscript{2}O on NO adsorption on the V\textsubscript{2}O\textsubscript{5}/AC catalysts, Huang et al. (2006) concluded that H\textsubscript{2}O did not influence NO adsorption on the surface of V\textsubscript{2}O\textsubscript{5}/AC. Therefore, we believe that water exerted an insignificant effect on NO adsorption on the surface of the alkaline-earth metal-doped C-FDU-15 samples.

Reusability of the typical samples was evaluated by carrying out the recycle experiments. Fig. S7 represents the RE values of the samples. A slight decrease in RE value was observed after five recycles. In the first recycle, the RE values of Mg-C-FDU-15(0.002) and C-FDU-15 were 91.7% and 97.5%, respectively. In the fifth recycle, the RE values of Mg-C-FDU-15(0.002) and C-FDU-15 were 86.3% and 94.6%, respectively. Apparently, the C-FDU-15 sample showed slightly better regeneration performance than the Mg-C-FDU-15(0.002) sample, which might be due to the negative effect of the residual Mg in the Mg-C-FDU-15(0.002) sample.

2.2.2. Texture of Mg-C-FDU-15(\(x\))

Shown in Fig. S8a are the wide-angle XRD patterns of the Mg-C-FDU-15(\(x\)) samples. Two peaks appeared at 2\(\theta\) = 26° and 44°, indicating that the Mg-C-FDU-15(\(x\)) samples were completely carbonized (Thamer et al., 2019). Compared with C-FDU-15, there were no obvious shifts in peak position of the Mg-C-FDU-15(\(x\)) samples, meaning that doping of Mg did not influence the carbonization degree of the material and the Mg was highly distributed in the sample (Ryou et al., 2018). Fig. S8b presents the low-angle XRD patterns of Mg-C-FDU-15(\(x\)), the recording of signals at 2\(\theta\) = 0.9° and 1.4° of Mg-C-FDU-15(\(x\)) (\(x = 0.001\) and 0.002) demonstrated the ordering of the samples (Xiao et al., 2015), while such signals were not obvious in the Mg-C-FDU-15(0.003) sample, a result possibly due to the destruction of regularity.

Fig. S9 shows TEM images of the Mg-C-FDU-15(\(x\)) samples. All of the samples preserved uniform parallel channels with a well-ordered 2D hexagonal mesostructure (p6mm) (Peng et al., 2016). Obviously, the orderliness of the Mg-C-FDU-15(\(x\)) samples was hardly changed as compared with that of C-FDU-15.

The N\textsubscript{2} isotherm method was used to investigate the porous structure of Mg-C-FDU-15(\(x\)) (Fig. 7a and b). As shown in Fig. 7a, N\textsubscript{2} sorption isotherms of the Mg-C-FDU-15(\(x\)) samples belonged to types I and IV, which was similar to that of the C-FDU-15 sample. The isotherms of the three samples showed a slight adsorption at low relative pressures, which was characteristic of micropores. In these four isotherms, hysteresis loops were observed at intermediate to high relative pressures, indicating the presence of mesopores (Yuan et al., 2018). Such a structure could provide enough space to promote the mass diffusion of NO and O\textsubscript{2}. As shown in Table 2, surface areas and pore volumes of the samples decreased with a rise in Mg content. As compared with the C-FDU-15 sam-

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**Fig. 5** – In situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) spectra of the surface species on the Ca-C-FDU-15(0.001) sample.

**Fig. 6** – TG profiles of (NO + O\textsubscript{2}) adsorption on the Mg-C-FDU-15(\(x\)) samples at 30°C.
ple, surface area decreased from 420 m²/g (C-FDU-15) to 318 m²/g (Mg-C-FDU-15(0.003)), and pore volume also slightly decreased from 0.28 cm³/g (C-FDU-15) to 0.26 cm³/g (Mg-C-FDU-15(0.003)), which could be attributed to the partial blocking of the channels in C-FDU-15 by MgO. Pore size distributions of the four samples are shown in Fig. 7b. In the case of C-FDU-15, there was co-existence of micropores and mesopores. When Mg was doped, the pore size increased from 2.68 (C-FDU-15) to 3.23 nm (Mg-C-FDU-15(0.003)). Fig. 7c presents the trend in (NO + O₂) adsorption, which first increased and then decreased, while surface area dropped, which illustrated that the adsorption of (NO + O₂) was little related to the surface area of each of the Mg-C-FDU-15(α) samples. That is to say, surface area was not a critical factor influencing the (NO + O₂) adsorption performance of the samples.

2.2.3. CO₂-TPD of Mg-C-FDU-15(α)
In the CO₂-TPD profile of the Mg-C-FDU-15(α) samples (Fig. 8a), three CO₂ desorption regions at 30–200, 200–290, and 380–420°C were ascribed to bicarbonate, bidentate carbonate and unidentate carbonate, respectively (Guo et al., 2020a). The sequence in amount of the basic sites (Table 2) was as follows: Mg-C-FDU-15(0.002) (277.8 mg/g) > Mg-C-FDU-15(0.001) (246.9 mg/g) > Mg-C-FDU-15(0.003) (175.4 mg/g) > C-FDU-15 (9.0 mg/g). Amount of the basic sites in the Mg-C-FDU-15(α) samples increased with a rise in Mg content. However, the surface area and pore volume continued to decrease with the addition of Mg, which led to the decrease in amount of the basic sites when Mg was excessively doped. Moreover, the LTP of C-FDU-5 was significantly increased after Mg doping, which indicated that Mg mainly improved the LTP of C-FDU-5. As can be seen from Fig. 8b, (NO + O₂) adsorption capacities of the Mg-C-FDU-15(α) samples were consistent with their amounts of the basic sites, which further proved that amount of the

Fig. 7 – (a) N₂ sorption isotherms, (b) pore diameter distributions, and (c) weight gain of (NO + O₂) and pore volumes of the Mg-C-FDU-15(α) samples.

Fig. 8 – (a) CO₂ desorption profiles and (b) weight gains (NO + O₂) and CO₂ of the Mg-C-FDU-15(α) samples.
basic sites was an important factor influencing the \((\text{NO} + \text{O}_2)\) adsorption performance.

2.2.4. \(\text{O}_2\)-TPD of Mg-C-FDU-15(x)

Fig. S10a shows \(\text{O}_2\)-TPD profiles of the Mg-C-FDU-15(x) samples, and their quantitative results are summarized in Table 2. The total amount of oxygen desorption decreased with a sequence of C-FDU-15 (2.61 mg/g) > Mg-C-FDU-15(0.003) (1.78 mg/g) ≈ Mg-C-FDU-15(0.002) (1.63 mg/g) ≈ Mg-C-FDU-15(0.001) (1.40 mg/g). Obviously, the amount of oxygen vacancies in Mg-C-FDU-15(x) was not significantly related to Mg addition. Furthermore, the amount of oxygen vacancies was inconsistent with the \((\text{NO} + \text{O}_2)\) adsorption performance of the Mg-C-FDU-15(x) sample (Fig. S10b). This result demonstrated that amount of oxygen vacancies was not the key factor influencing the \((\text{NO} + \text{O}_2)\) adsorption performance of the samples. Similar to A-C-FDU-15, adsorption capacity of \(\text{O}_2\) was much lower than that of \((\text{NO} + \text{O}_2)\) on Mg-C-FDU-15(x), which implied that \(\text{O}_2\) was not the main adsorption species in the adsorption of \((\text{NO} + \text{O}_2)\).

2.3. Mechanism of \((\text{NO} + \text{O}_2)\) adsorption on Mg-C-FDU-15(x)

2.3.1. \((\text{NO} + \text{O}_2)\)-TPD of Mg-C-FDU-15(x)

Fig. 9 shows the \((\text{NO} + \text{O}_2)\)-TPD profiles and their fitting curves of the Mg-C-FDU-15(x) samples. Same as A-C-FDU-15, there were three nitro species of \(\text{NO}_2\), nitrates, and nitrates at 30–400°C. Amount of \(\text{NO}_2\) desorption was calculated by curve-fitting (Fig. S11 and Table 3). The sequence in \(\text{NO}_x\) desorption was as follows: Mg-C-FDU-15(0.002) (72.1 mg/g) > Mg-C-FDU-15(0.001) (68.7 mg/g) > Mg-C-FDU-15(0.003) (62.6 mg/g) > C-FDU-15 (53.0 mg/g). It was obvious that amount of the \(\text{NO}_2\) desorption from the Mg-C-FDU-15(x) samples was more than that from C-FDU-15, with the Mg-C-FDU-15(0.002) sample desorbing the highest amount of \(\text{NO}_x\), which was consistent with the adsorption of \((\text{NO} + \text{O}_2)\). This result further demonstrated that a proper amount of alkaline earth metal doping also played an important role in the adsorption of \((\text{NO} + \text{O}_2)\).

2.3.2. \(\text{DRIFTS of} \ (\text{NO} + \text{O}_2) \ \text{adsorption on Mg-C-FDU-15(x)}\)

DRIFTS spectra of the Mg-C-FDU-15(0.001) sample are shown in Fig. 10 and those of the Mg-C-FDU-15(x) samples are presented in Fig. S12. Same as A-C-FDU-15(0.001) and C-FDU-15, five absorption bands at 833, 1356, 1390, 1415, and 1434 cm\(^{-1}\) (Fig. 10) appeared for the Mg-C-FDU-15(0.001) sample, which corresponded to the chelating nitrite, adsorbed nitrate, free nitrate, linear nitrite, and nitro compounded nitrite. Thus, the formed species by \((\text{NO} + \text{O}_2)\) adsorption were not affected after doping of various amounts of the alkaline earth metals. DRIFTS spectra (Fig. S12c and d) of \((\text{NO} + \text{O}_2)\) adsorption on Mg-C-FDU-15(0.002) and Mg-C-FDU-15(0.003) were similar to those on Mg-C-FDU-15(0.001) (Fig. S12a). All of the bands were observed almost at the same positions, indicating that Mg exerted no impact on formation of the nitro species via adsorption. However, the sequence in band intensity decreased according to Mg-C-FDU-15(0.002) > Mg-C-FDU-15(0.001) > Mg-C-FDU-15(0.003) > C-FDU-15. \((\text{NO} + \text{O}_2)\) adsorption capacity of Mg-C-FDU-15(0.002) was the largest among the four samples, which was consistent with the outcomes of the TG and \((\text{NO} + \text{O}_2)\)-TPD characterization. It might be due to the change in amount of the basic sites in the Mg-C-FDU-15(x) samples, resulting in a significant increase in intensity of the band.

2.3.3. Mechanism

Usually, the samples with strong redox sites exhibit good catalytic performance for the oxidation of NO to \(\text{NO}_2\) (Pan et al., 2017; Fang et al., 2019). The NO oxidation experiment of Mg-C-FDU-15(0.002) was performed and the results are shown in Fig. S13. Apparently, NO could be oxidized to \(\text{NO}_2\) by \(\text{O}_2\) over the Mg-C-FDU-15(0.002) sample. The adsorbed oxygen species and/or oxygen free radicals could react with NO to form \(\text{NO}_2\), which was adsorbed on the surface of the A-C-FDU-15 samples and transformed to the \(\text{NO}_2^-\) and \(\text{NO}_3^-\) species. According to the basic site characterization, there were three kinds of
basic sites in the samples. One was the surface hydroxyl of carbon material, which could adsorb a large number of NO$_2$ converted from (NO + O$_2$). The other two were strong adsorption sites, which convert (NO + O$_2$) to NO$_2^-$ and NO$_3^-$. Meanwhile, introducing an alkaline earth metal to C-FDU-15 also played a crucial role in promoting the conversion of NO to NO$_2$. Alkaline earth atoms promoted the formation of more hydroxyl groups on the surface of carbon, thus leading to enhancement in adsorption performance of the samples (Xie et al., 2019; Li et al., 2018). Two main adsorption pathways might occur during the (NO + O$_2$) adsorption process (Fig. S14).

Since NO$_2$ was easily converted after mixing of NO and O$_2$. A large amount of NO$_2$ was formed in the adsorption of (NO + O$_2$), and one part of NO$_2$ was weakly adsorbed on the surface hydroxyl groups of carbon material, the other part of NO$_2$ reacted with the active sites of carbon material to form NO$_3^-$. Some of the NO$_3^-$ species decomposed into the oxygen-containing functional groups of carbon due to its instability, the other part of NO$_3^-$ and oxygen free radicals was converted to the stable NO$_3^-$. The possible mechanisms were as follows:

$$\text{O}_2(\text{g}) \rightarrow 2 \text{O(ad)}$$  \hspace{1cm} (1)

$$\text{NO} + \text{O(ad)} \rightarrow \text{NO}_2$$  \hspace{1cm} (2)

$$\text{C-C} + \text{NO}_2 \rightarrow \text{C-NO}_2 + \text{C}$$  \hspace{1cm} (3)

$$\text{C-NO}_2 + \text{C-NO}_2 \rightarrow \text{C-NO}_3 + \text{C} + \text{NO}$$  \hspace{1cm} (4)

$$\text{C-NO}_2 \rightarrow \text{C} + \text{NO}$$  \hspace{1cm} (5)

$$\text{NO}_2 + \text{C-O} \rightarrow \text{C-NO}_3$$  \hspace{1cm} (6)

Another possible pathway was that the edge of carbon materials was easy to form the oxygen-containing functional groups. In other words, two oxygen atoms decomposed by O$_2$ could generate the oxygen functional groups at the active sites, then the oxygen functional groups reacted with NO to produce nitrite (NO$_2^-$) species. Meanwhile, part of NO$_2^-$ was oxidized to NO$_3^-$ species by oxygen free radicals, and the other NO$_3^-$ species reacted with each other to produce NO$_3^-$ and NO. In addition, nitrate was directly produced by the reaction of NO with the oxygen atoms or active oxygen on the surface of carbon materials. The possible mechanisms are as follows:

$$\text{O}_2(\text{g}) \rightarrow 2 \text{O(ad)}$$  \hspace{1cm} (1)

$$\text{C-C} + 2 \text{O(ad)} \rightarrow 2 \text{C-O}$$  \hspace{1cm} (7)

$$\text{NO} + \text{C-O} \rightarrow \text{C-NO}_2$$  \hspace{1cm} (8)

$$\text{C-NO}_2 + \text{C-O} \rightarrow \text{C-NO}_3 + \text{C} + \text{NO}$$  \hspace{1cm} (9)

$$\text{C-NO}_2 + \text{C-NO}_2 \rightarrow \text{C-NO}_3 + \text{C} + \text{NO}$$  \hspace{1cm} (4)

$$\text{NO} + \text{C-O} \xrightarrow{\text{O}_2{^{\text{ad}}}} \text{C-NO}_3$$  \hspace{1cm} (10)

2.4. Adsorption kinetics

Adsorption kinetics was used to investigate the rate-controlling steps and reaction pathways. The data of the various Mg-C-FDU-15(x) samples were fitted with the following two models to analyze the influence of Mg doping on sorption kinetics (Raganati et al., 2019; Chen et al., 2014):

$$\lg(Q_e - Q_i) = \lg(Q_e - m_1 t/2)$$  \hspace{1cm} (11)

$$Q_t = \frac{m_2 Q_e^2 t}{1 + m_2 Q_e^2 t}$$  \hspace{1cm} (12)

where $Q_e$ (mg/g) is the adsorption capacity in equilibrium, $Q_i$ (mg/g) is the adsorption capacity at particular time (t), t is the particular time in adsorption and $m_1$ (mg/(g·min)) and $m_2$ (mg/(g·min)) are the rate constants of the two models, respectively.

Fig. S15 and Table 4 show the fitting curves and parameters of the two kinetic models, respectively. The $R^2$ value of the first model was between 0.89 and 0.97, whereas the $R^2$ value of the second model was between 0.98 and 1.00. It was obvious that the fitting quality of the second model was almost consistent with the experimental data. Generally, the first model is suited to describe a pure physical adsorption process, while the second model is suited to describe a chemical adsorption process. Therefore, most of the adsorption was chemisorption on the samples, i.e., chemisorption might be a rate-limiting step in the adsorption process.

The Weber–Morris model was introduced to investigate the interparticle diffusion, as described below:

$$Q_t = n t^{1/2} + C$$  \hspace{1cm} (13)

where $n$ (mg/(g·min$^{1/2}$)) is the intraparticle diffusion constant, and $C$ (mg/g) is the intercept (reflecting the thickness of diffusion boundary layer).

Fig. S16 shows the fitting curves of the intragranular diffusion kinetic model of Mg-C-FDU-15(x) and C-FDU-15. The plots showed several steps in NO + O$_2$ adsorption. The process could be divided into three stages: the external fluid film diffusion, intraparticle diffusion, and reaction process (Banerjee et al., 2019). During the external fluid film diffusion, sufficient active sites in the samples were needed to ensure the rapid increase of adsorption. Then the adsorption remained increased slowly, which was attributed to weakening of the adsorption force caused by the decrease in concentration difference with the extension of time. During the adsorption of (NO + O$_2$), the active center became more and more saturated and the adsorption reached an equilibrium. It was worth noting that the linear sections did not pass through the origin of the fitted curves, which confirmed that the intraparticle diffusion was never the sole stage controlling the rate of (NO + O$_2$) adsorption. Therefore, the three different processes controlled the adsorption rate within the specific time. The trends of the four samples (Fig. S15) were similar, however, the slope of Mg-C-FDU-15(0.002) was higher than those of the other samples in film diffusion (Table 5), which indicated that the increase in diffusion rate was the most significant in Mg-C-FDU-15(0.002). In the reaction process, the slope of Mg-C-FDU-15(0.002)
Table 4 – Parameters of the kinetic models of (NO + O₂) adsorption on the Mg-C-FDU-15(α) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pseudo first-order</th>
<th></th>
<th>Pseudo second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Qₐ</td>
<td>m₁</td>
<td>R²</td>
</tr>
<tr>
<td>C-FDU-15</td>
<td>94.95</td>
<td>0.021</td>
<td>0.89</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.001)</td>
<td>96.21</td>
<td>0.02</td>
<td>0.96</td>
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<tr>
<td>Mg-C-FDU-15(0.002)</td>
<td>108.86</td>
<td>0.02</td>
<td>0.97</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.003)</td>
<td>94.60</td>
<td>0.02</td>
<td>0.95</td>
</tr>
</tbody>
</table>

a Qₑ (mg/g): the adsorption capacity in equilibrium;  
b m₁ (mg/(g·min)): the rate constants of the first model;  
c mₑ (mg/(g·min)): the rate constants of the second model.

Table 5 – Kinetic parameters obtained using the Weber–Morris model of (NO + O₂) adsorption on the Mg-C-FDU-15(α) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>First-portion</th>
<th></th>
<th>Second-portion</th>
<th></th>
<th>Third-portion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nₑ⁻¹</td>
<td>Cₑ⁻¹</td>
<td>R²</td>
<td>nₑ⁻¹</td>
<td>Cₑ⁻¹</td>
</tr>
<tr>
<td>C-FDU-15</td>
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<td>72.09</td>
<td>0.99</td>
<td>0.73</td>
<td>82.33</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.001)</td>
<td>1.99</td>
<td>67.20</td>
<td>0.99</td>
<td>0.92</td>
<td>81.02</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.002)</td>
<td>2.44</td>
<td>79.85</td>
<td>0.99</td>
<td>0.87</td>
<td>94.31</td>
</tr>
<tr>
<td>Mg-C-FDU-15(0.003)</td>
<td>2.01</td>
<td>65.03</td>
<td>0.99</td>
<td>0.74</td>
<td>81.79</td>
</tr>
</tbody>
</table>

a nₑ (mg/(g·min)⁻¹): the intraparticle diffusion constant;  
b Cₑ (mg/g): the intercept (reflecting the thickness of diffusion boundary layer).

15(0.002) was less than that of Mg-C-FDU-15(0.003), meaning that Mg doping produced a more amount of the basic sites in Mg-C-FDU-15(0.003), and a more amount of chemical adsorption occurred during the adsorption process.

3. Conclusions

In this work, the influence of the A-C-FDU-15(α) samples on (NO + O₂) adsorption at low temperatures was investigated. When the C-FDU-15 was doped with the alkaline earth metals, (NO + O₂) adsorption was improved and the sequence was as follows: Mg-C-FDU-15(0.001) > Ca-C-FDU-15(0.001) > Sr-C-FDU-15(0.001) > Ba-C-FDU-15(0.001) > C-FDU-15. It was found that the species of alkaline earth metals was the decisive factor influencing the (NO + O₂) adsorption, and the Mg-C-FDU-15(0.002) sample showed the best (NO + O₂) adsorption performance. Amount of the basic sites was also an important factor influencing the adsorption of (NO + O₂).

Combined with the analysis of DRIFTS spectra and (NO + O₂)-TPD profiles, two main adsorption pathways in the process of (NO + O₂) adsorption were presented: one was the conversion of NO and O₂ to a large amount of NO₂, in which part of NO₂ was weakly adsorbed on the surface hydroxyl groups, the other part of NO₂ was converted to NO₃⁻, followed by the conversion of NO₂⁻ to NO₃⁻. The other pathway was that NO was directly oxidized to NO₂⁻ by the oxidized carbon functional groups, and then some NO₂⁻ was converted to NO₃⁻. Through the kinetic analysis of (NO + O₂) adsorption, the adsorption was mainly chemical adsorption. Moreover, the three stages — film diffusion, particle internal diffusion and final equilibrium, can all affect the rate of adsorption.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.10.014.

REFERENCES


