

Mechanism of enhancing NH_3 -SCR performance of Mn-Ce/AC catalyst by the structure regulation of activated carbon with calcite in coal

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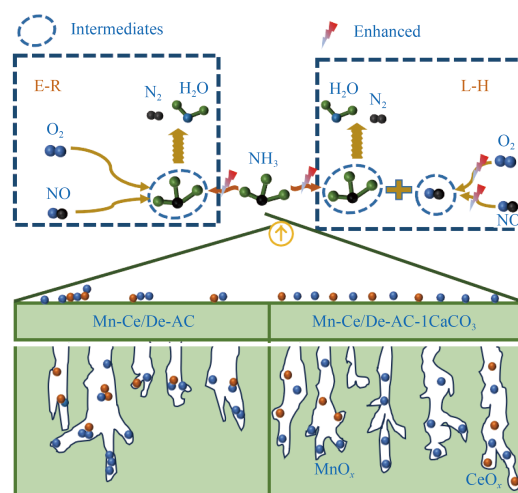
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Abstract: To elucidate the effect of calcite-regulated activated carbon (AC) structure on low-temperature denitrification performance of SCR catalysts, this work prepared a series of Mn-Ce/De-AC- $x\text{CaCO}_3$ (x is the calcite content in coal) catalysts were prepared by the incipient wetness impregnation method, followed by acid washing to remove calcium-containing minerals. Comprehensive characterization and low-temperature denitrification tests revealed that calcite-induced structural modulation of coal-derived AC significantly enhances catalytic activity. Specifically, NO conversion increased from 88.3% of Mn-Ce/De-AC to 91.7% of Mn-Ce/De-AC-1 CaCO_3 (210 °C). The improved SCR denitrification activity results from the enhancement of physicochemical properties including higher Mn^{4+} content and $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio, an abundance of chemisorbed oxygen and acidic sites, which could strengthen the SCR reaction pathways (richer NH_3 activated species and bidentate nitrate active species). Therefore, NO removal is enhanced.

Key words: calcite; activated carbon; structure; Mn-Ce/AC catalyst; NH_3 -SCR performance



As one of the major atmospheric pollutants, the massive emissions of nitrogen oxides (NO_x) could cause serious environmental issues such as nitric acid rain, greenhouse effect and photochemical smog, etc., meanwhile, threatening human health. Among various NO_x removal techniques, selective catalytic reduction with ammonia (NH_3 -SCR) is mainstream technology for flue gas denitrification, which is currently the most widely and effectively applied in coal-fired power plants. However, the narrow operating temperature window of conventional

$\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ catalysts (300–400 °C) limits their broader application in non-electric industries (generally below 250 °C)^[1–2]. Consequently, developing cost-effective and high-performance low-temperature SCR catalysts has emerged as a research hotspot.

Transition metals are frequently employed as active components for the preparation of low-temperature SCR catalysts owing to their strong redox ability and variable valence states, such as manganese (Mn) and cerium (Ce)^[3]. Current research focuses on enhancing low-temperature

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denitrification activity of the SCR catalysts by the synergistic effect of active components. Previous studies proved that the synergistic effect of Mn and Ce could significantly enhance the denitrification performance of SCR catalysts^[4–5]. Additionally, suitable support is a critical aspect for preparing high-performance SCR catalysts. Carbon-based materials can serve as support and catalyst simultaneously, especially activated carbon (AC)^[6–7]. The well-developed pore structure and abundant surface functional groups of AC could serve as active sites for enhancing NH_3 adsorption and activation, meanwhile, which could facilitate electron transfer and further adjust electronic structures and valence states of active species, enabling efficient reduction of NO_x to N_2 , hence achieving flue gas purification^[8]. AC-based low-temperature SCR catalysts have been the most widely applied in low-temperature flue gas purification, suggesting broad application potential.

Structural characteristics of AC affect the dispersion of active components and thus determine the low-temperature denitrification activity of the SCR catalysts^[9]. Optimization of AC texture by adjusting preparation conditions could enhance the interaction effect of support and active components, hence improving low-temperature SCR activity^[10]. Previous studies investigated the relationship between AC texture and low-temperature activity of SCR catalysts. The results show that defect engineering via activation time optimization promotes metal dispersion and enhances catalytic performance^[11]. Furthermore, the composition of coal could influence the AC structure, which also affects SCR catalytic denitrification behavior. However, there are nearly no studies about the effect of coal composition on the denitrification performance of SCR catalysts. As a major component in coal, inorganic mineral matters such as calcite can influence AC structure development^[12–13]. During AC preparation at 900 °C, calcite could transform into CaO, which could react with CO_2 in the cooling gas to form CaCO_3 . Calcite in coal promotes decomposition of carbon matrix, catalyzes steam and CO_2 co-activation and reduces graphitization degree. Calcite in coal promotes micro- to meso-pore transformation or pore collapse, the total specific surface area and micropore specific surface area decrease from 1398 and 517 m^2/g to 1292 and 451 m^2/g , respectively. Meanwhile, calcite enhances surface oxygen-containing functional groups of AC including C=O, COO, π - π ^[12]. Clarifying the impact and mechanism of the AC structure regulated by calcite in coal on the denitrification performance of SCR catalysts could provide critical guidance for developing high-performance catalysts derived from high-calcium coal. Nevertheless, the influence of calcite-regulated AC structure on low-temperature denitrification activity of the SCR catalyst is still unclear.

Therefore, to unveil the effect of AC regulated by calcite in coal on low-temperature denitrification performance of SCR catalysts, this work prepared Mn/De-AC- $x\text{CaCO}_3$ or Mn-Ce/De-AC- $x\text{CaCO}_3$ (where x is the content of calcite in coal) catalyst through acid-washing followed by incipient wetness impregnation and calcination. The active

components are fixed at 5% Mn or Mn-Ce (mass ratio of 7:3). The role of AC texture regulated by calcite in coal on the SCR catalysts was achieved by a series of characterization including BET, XRD, Raman, XPS and *in situ* DRIFTS. The results of this work could provide critical theoretical support and technical guidance for utilizing high calcium coal to construct high-performance low-temperature SCR catalysts.

1 Experimental

1.1 Catalyst preparation

1.1.1 Preparation of demineralized AC

Consistent with our previous methodology, AC- $x\text{CaCO}_3$ (x represents calcite content in coal, %) was successfully synthesized by blending CaCO_3 and demineralized Taixi coal^[12]. To obtain the mechanistic effect of AC structure regulated by calcite in coal on the denitrification activity of SCR catalysts, the calcium-containing minerals including CaCO_3 and CaO in AC required removal and the structure should not undergo change. Demineralized AC (remarked as De-AC- $x\text{CaCO}_3$, where x represents the content of calcite in coal) was produced by first immersing AC- $x\text{CaCO}_3$ in 1 mol/L HCl for 48 h at ambient temperature, and followed by washing with deionized water for 7–10 times until up to neutral (pH=6.8–7.2). The results of XRD and ICP analyses confirmed that this method successfully removal calcium-containing minerals in AC (Figure 1).

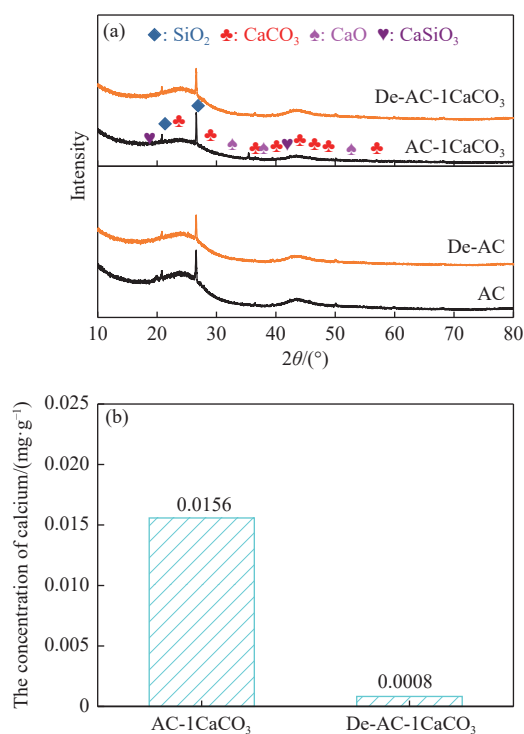


Fig. 1 XRD patterns and ICP results of AC after/before acid-washing

XRD results indicated that there are no obvious peaks of CaCO₃ and CaO in AC after acid-washing (Figure 1(a)). ICP results also showed that acid-washing almost completely removed the calcium-containing minerals in AC (Figure 1(b)). Above results both proved that demineralized AC was successfully achieved.

1.1.2 Preparation of SCR catalyst

The SCR catalyst was prepared by the incipient wetness impregnation method and loaded with 5% Mn and Mn-Ce (mass ratio of 7:3) in demineralized AC. Firstly, adding demineralized AC support to the solution with Mn(NO₃)₂ and/or Ce(NO₃)₂ and subjected to ultrasonic treatment (200 W, 40 kHz) for 1 h, then place it for 48 h. Finally, after drying, the precursors were calcined from ambient temperature to 400 °C for 2 h at a heating rate of 10 °C/min under a high-purity nitrogen (99.999%). The SCR catalysts were remarked as Mn/De-AC-*x*CaCO₃, Mn-Ce/De-AC-*x*CaCO₃, where *x* represents the content of calcite in coal (%).

1.2 Characterization

The content of Ca in AC before/after acid-washing was determined by inductively coupled plasma atomic emission spectrometry (ICP-OES). The Raman spectrum of the catalyst was obtained by using the Raman spectrometer (LabRAM HR evolution, France). Incident wavelength of $\lambda=632.8$ nm (Nd: YAG laser), laser power 20 MW, scanning range 500–2000 cm⁻¹, spectrum collection time 60 s. The morphology of the SCR catalyst was tested by scanning electron microscope (JSM-IT500HR, Japan). Meanwhile, the surface chemical composition of the catalyst sample was obtained by X-ray energy dispersive spectroscopy (EDS). The pore structure parameters of the SCR catalyst were measured by Quantachrome ASiQwin. The surface functional groups of the SCR catalyst were characterized by Fourier transform infrared spectroscopy (FT-IR). The surface chemistry of the SCR catalyst was tested by X-ray photoelectron spectroscopy (XPS), and all XPS curves were calibrated according to the C 1s peak (284.8 eV). The NO removal performance of the SCR catalyst was obtained by NO+O₂ temperature programmed desorption (NO+O₂-TPD). 100 mg SCR catalyst samples were put into a self-made fixed-bed reactor and heated to 300 °C in N₂ atmosphere for 1 h to remove the impurities physically adsorbed on the catalyst surface. When the temperature of the SCR catalyst was decreased to 50 °C, 200 mL of mixed gas (including 5% O₂ and 1.0×10⁻³ NO and N₂ balance) was introduced and held for 1 h until adsorption is saturated, and then purged with N₂ for 30 min. Finally, the catalyst sample was heated to 500 °C with a heating rate of 10 °C/min and a flow rate of 200 mL of N₂. Desorption curves of NO and NO₂ with temperature were recorded by a Vario Plus flue gas analyzer (MRU). *In situ* diffuse reflectance infrared Fourier transform spectra (*in*

situ DRIFTS) of the SCR catalyst were obtained by a Fourier transform infrared absorption instrument. Before the test, the SCR catalyst sample was pretreated and heated to 200 °C for 2 h in a N₂ atmosphere at the heating rate of 10 °C/min. The SCR catalyst sample was put into the *in situ* gas pool and heated to 120 °C at a heating rate of 10 °C/min. After purging in Ar atmosphere for 30 min, the background was collected, NH₃ (1.0×10⁻³) was introduced, Ar was used as the balance gas, and the *in situ* infrared spectrum was collected for 30 min. After the end of purging for 30 min (Ar atmosphere), NO (1.0×10⁻³) and O₂ (Ar is used as the balance gas) were introduced, and *in situ* infrared spectrum was collected for 30 min. The acquisition time interval was 1 min. The spectral resolution is 8 cm⁻¹, the number of scans is 64, and the acquisition range is 1000–4000 cm⁻¹.

1.3 Denitrification activity evaluation

The denitrification performance of SCR catalysts was achieved by the custom-made fixed-bed microreactors. For each testing, 1 mL of SCR catalyst was placed into reactors and then using simulated flue gas (5.0×10⁻⁴ NO, 5.0×10⁻⁴ NH₃, 5% O₂ and N₂ balance) to evaluate. The concentrations of outlet gas (including NO, N₂O, NH₃ and O₂) were continuously monitored by a 9100FIR flue gas analyzer. The GHSV (gas hourly space velocity) and temperature are 12000 h⁻¹ and 90–240 °C, respectively. The NO conversion and N₂ selectivity were calculated by the following formulas (1) and (2), respectively.

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

$$s_{\text{N}_2} = \left[1 - \frac{2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NH}_3]_{\text{in}} + [\text{NO}]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}]_{\text{out}}} \right] \times 100\% \quad (2)$$

where by subscripts [NO]_{in}, [N₂O]_{in}, [NH₃]_{in}, [NO]_{out}, [N₂O]_{out} and [NH₃]_{out} denote inlet and outlet concentrations of NO, N₂O and NH₃. Tests were repeated 3–5 times for statistical reliability.

2 Results and discussion

2.1 Denitrification activity of the SCR catalyst

Denitrification activities of Mn/De-AC-*x*CaCO₃ and Mn-Ce/De-AC-*x*CaCO₃ catalysts are shown in Figure 2. Results show that the NO conversion of SCR catalysts increased with increasing temperature. When the temperature was increased from 90 to 240 °C, the NO conversion of Mn-Ce/De-AC catalyst was significantly higher than that of Mn/De-AC catalyst, which increased from 18.6% (90 °C), 44.5% (180 °C), and 80.1% (240 °C) to 26.9% (90 °C), 67.7% (180 °C), and 91.9% (240 °C), respectively. This is mainly due to the synergistic effect of Mn-Ce^[4].

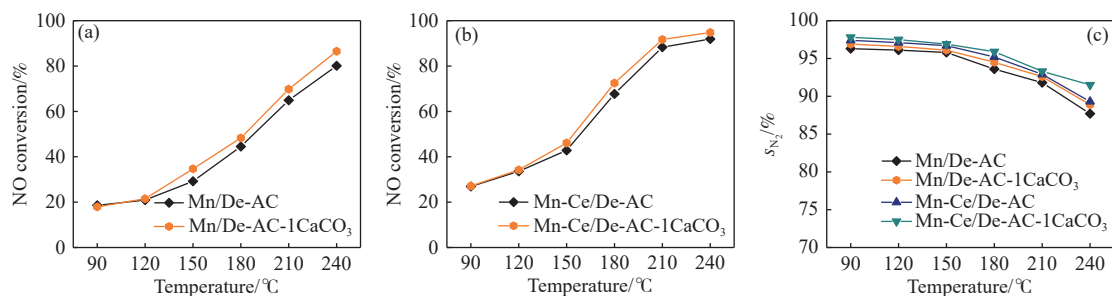


Fig. 2 The SCR activity of catalysts (a), (b) and N_2 selectivity (c) at low temperatures

Meanwhile, Mn/De-AC-1CaCO₃ and Mn-Ce/De-AC-1CaCO₃ catalysts exhibited higher denitrification activities compared to Mn/De-AC and Mn-Ce/De-AC-1CaCO₃, respectively. When the temperature arrived at 120 and 210 °C, NO conversion of the SCR catalysts achieved 34.7% and 69.8% (Mn/De-AC-1CaCO₃) and 46.1% and 91.7% (Mn-Ce/De-AC-1CaCO₃), which is higher than 29.2% (120 °C) and 64.9% (210 °C) for the Mn/De-AC and 42.8% (120 °C) and 88.3% (210 °C) for the Mn-Ce/De-AC. Meanwhile, the AC structure regulated by calcite in coal enhanced N_2 selectivity of the SCR catalysts. The main reason for the enhanced denitrification activity of the SCR catalysts may be that the AC structure regulated by calcite in coal is favorable for the dispersion of Mn-Ce. The enhancement effect of the AC structure regulated by calcite in coal on the denitrification performance of SCR catalysts was obtained in following sections.

2.2 Crystalline structure

To elucidate the effect of the AC structure regulated by

calcite in coal on the defects of the SCR catalysts, Raman spectroscopy was employed (Figure 3). SCR catalysts mainly exhibited a G peak and a D peak. The G peak is caused by in-plane vibration of the sp^2 atoms in the carbon ring or the long chain and is located near 1580 cm^{-1} . The D peak is due to the disordered vibration of the low graphitization degree carbon and is located near 1350 cm^{-1} , which is generally used to characterize structural defects or edges in carbon materials^[12]. SCR catalysts obtained based on the AC structure regulated by calcite in coal possessed abundant defects. The defect intensity (I_D) of Mn/De-AC-1CaCO₃ reached 7890, which was higher than that of 7362 for Mn/De-AC. Meanwhile, the I_D of Mn-Ce/De-AC-1CaCO₃ was 7890, which was also higher than that of 7693 for the Mn-Ce/De-AC. SCR catalysts show abundant defects due to AC structure regulated by calcite in coal favors the dispersion of Mn/Mn-Ce, such as the increase of oxygen-containing functional groups containing C=O^[14]. Rich defects on the surface of the SCR catalysts favor the adsorption and activation of NO, thus promoting SCR reaction^[15].

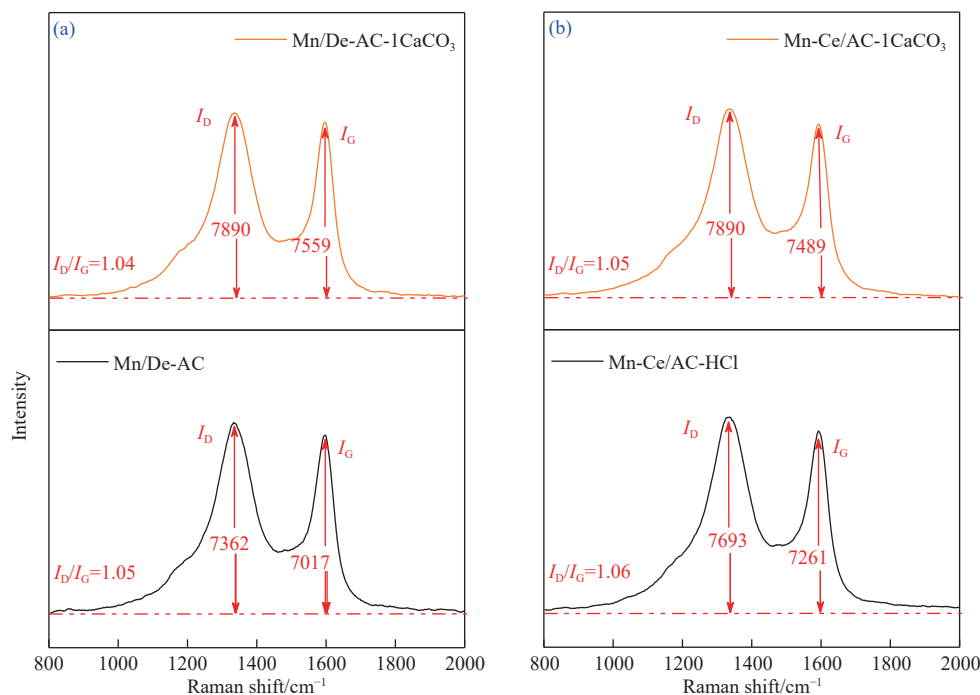


Fig. 3 Raman spectra of Mn/De-AC- $x\text{CaCO}_3$ (a) and Mn-Ce/De-AC- $x\text{CaCO}_3$ (b) catalysts

2.3 Pore structure

The nitrogen adsorption and desorption curves and pore size distributions of Mn/De-AC- $x\text{CaCO}_3$ and Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts are shown in Figure 4. The nitrogen adsorption and desorption curves of the SCR catalysts exhibited typical type I and type IV isotherms^[16–17]. It can be seen that N_2 adsorption of the catalysts increased significantly when $p/p_0 < 0.01$. N_2 adsorption of the catalysts gradually became flat. When the $p/p_0 > 0.01$ (Figure 4(a) and (c)), the Mn/De-AC- $x\text{CaCO}_3$ and Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts were microporous materials. These results indicate few differences in the pore structure of the SCR catalyst exists. Pore size distribution plots illustrated that the differences between the pore sizes of SCR catalysts were mainly concentrated in the micropores, especially in the 0.5–2 nm range. There were also few differences in the mesopores of SCR catalysts, such as 2–10 nm (Figure 4(b)

and (d)).

The pore structure parameters of Mn/De-AC- $x\text{CaCO}_3$ and Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts are shown in Table 1. The specific surface area and pore volume of Mn/De-AC- $x\text{CaCO}_3$ are also similar to Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts. The total specific surface area, microporous specific surface area, and macropore and mesopore specific surface area of the Mn/De-AC- $x\text{CaCO}_3$ catalysts were 1058–1013, 497–573 and 561–440 m^2/g , respectively. The total, microporous, and macropore and mesopore volumes of the Mn/De-AC- $x\text{CaCO}_3$ catalysts were 0.532–0.547, 0.203–0.229 and 0.329–0.318 cm^3/g , respectively. The average pore size of Mn/De-AC- $x\text{CaCO}_3$ catalysts increased from 2.013 to 2.126 nm. The total specific surface area, microporous specific surface area, and macropore and mesopore specific surface area of the Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts were 1186–1154, 418–507 and 768–647 m^2/g , respectively.

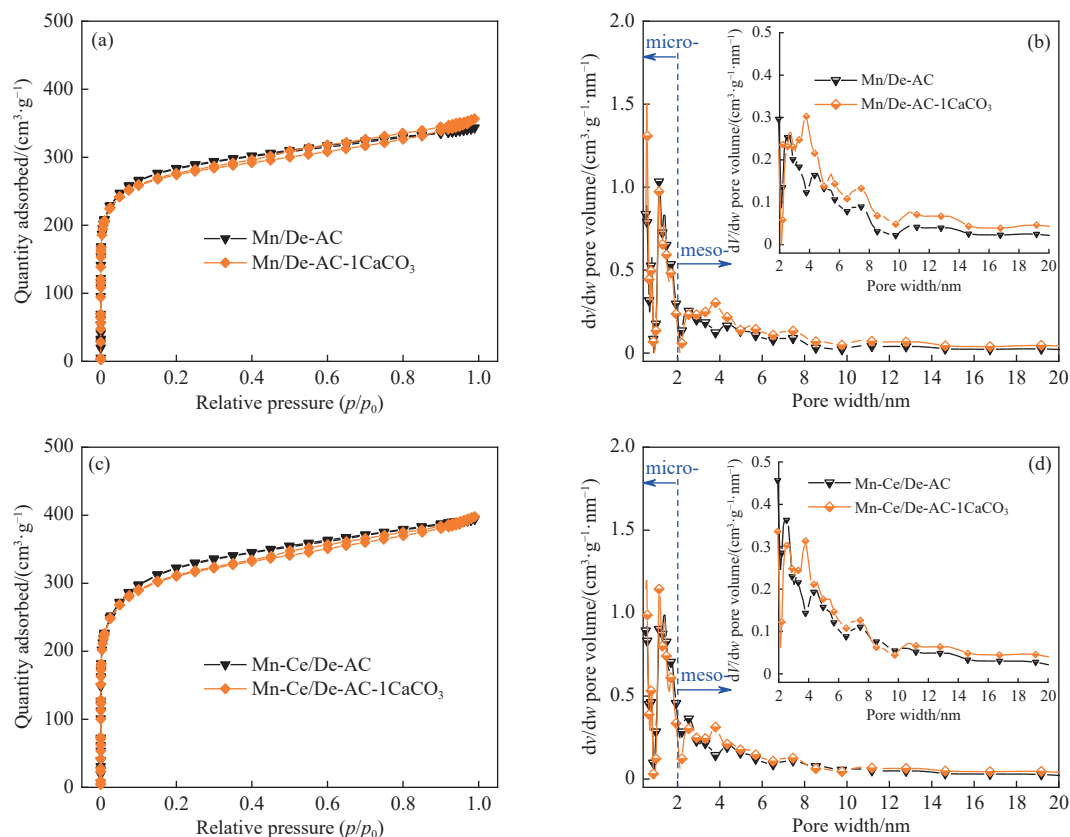


Fig. 4 Adsorption-desorption isotherms of nitrogen (a) Mn/De-AC- $x\text{CaCO}_3$; (c) Mn-Ce/De-AC- $x\text{CaCO}_3$ and pore size distribution (b) Mn/De-AC- $x\text{CaCO}_3$; (d) Mn-Ce/De-AC- $x\text{CaCO}_3$ of SCR catalysts

Table 1 Porosity parameters of Mn/De-AC- $x\text{CaCO}_3$ and Mn/De-AC- $x\text{CaCO}_3$ catalysts

Sample	Pore structure parameters						
	S_{mic}^2 /($\text{m}^2 \cdot \text{g}^{-1}$)	S_{ext}^2 /($\text{m}^2 \cdot \text{g}^{-1}$)	S_{BET}^2 /($\text{m}^2 \cdot \text{g}^{-1}$)	v_{total}^3 /($\text{cm}^3 \cdot \text{g}^{-1}$)	v_{mic}^3 /($\text{cm}^3 \cdot \text{g}^{-1}$)	v_{ext}^3 /($\text{cm}^3 \cdot \text{g}^{-1}$)	d_{ave} /nm
Mn/De-AC	497	561	1058	0.532	0.203	0.329	2.013
Mn/De-AC-1CaCO ₃	573	440	1013	0.547	0.229	0.318	2.126
Mn-Ce/De-AC	418	768	1186	0.612	0.176	0.436	2.062
Mn-Ce/De-AC-1CaCO ₃	507	647	1154	0.616	0.207	0.409	2.134

The total pore volume, microporous pore volume, and macropore and mesopore volume of the Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts were 0.612–0.616, 0.176–0.207 and 0.436–0.409 cm^3/g , respectively. Similarly, the average pore size of the Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts increased from 2.062 to 2.134 nm. The high specific surface area and pore volume of the SCR catalysts, which can be used as active sites, promote adsorption and conversion of NO_x , NH_3 and O_2 , and ultimately promote SCR reaction. Overall, the pore structure is not the major reason for the difference in SCR performance of SCR catalysts because the Mn/De-AC- $x\text{CaCO}_3$ catalysts and the Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts have similar specific surface area and pore volume.

2.4 Morphology

The morphology of Mn/De-AC- $x\text{CaCO}_3$ and Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts is shown in Figure 5. Mn/De-AC- $x\text{CaCO}_3$ and Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts have smoother surfaces, which is mainly due to the incipient wetness impregnation reshaping their smooth surfaces (Figure 5(a)–(d)). EDS analysis showed the presence of MnO_x on the surface of Mn/De-AC (Figure 5(b)). Meanwhile, abundant pore structures on the surface of the Mn/De-AC-1 CaCO_3 catalyst were found (Figure 5(c)). Compared with Mn-Ce/De-AC catalyst, relatively rougher surface of the Mn-Ce/De-AC-1 CaCO_3 was found, which is

mainly determined by the rougher surface of the De-AC- $x\text{CaCO}_3$ catalyst (Figure 5(d) and (e))^[18]. The presence of CeO_x was observed on the surface of the Mn-Ce/De-AC- $x\text{CaCO}_3$ catalyst (Figure 5(f)). It should be noticed that Mn/De-AC- $x\text{CaCO}_3$ and Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts do not have Ca, which validates that the present experiment successfully removed the calcium-containing minerals in AC. Thus, it can intuitively reflect the influence of the AC structure regulated by calcite in coal on denitrification performance of the SCR catalyst.

2.5 Surface chemistry

FT-IR analyses of Mn/De-AC- $x\text{CaCO}_3$ and Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts are presented in Figure 6. The peaks at 3700–3000 cm^{-1} are attributed to O–H stretching vibrations. The peak at 3000–2700 cm^{-1} is attributed to C–H stretching vibrations^[19]. The peak at 1800–1000 cm^{-1} is attributed to C=O and C–O stretching vibrations^[20].

To further investigate the effect of the calcite-regulated AC structure on the surface elemental species and their valence states, XPS was conducted on the Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts were analyzed by XPS. XPS survey spectra (a), Mn 2p (b), Ce 3d (c) and O 1s spectra (d) of the SCR catalysts are presented in Figure 7, respectively, and the relative contents of each component of the SCR catalysts are shown in Table 2.

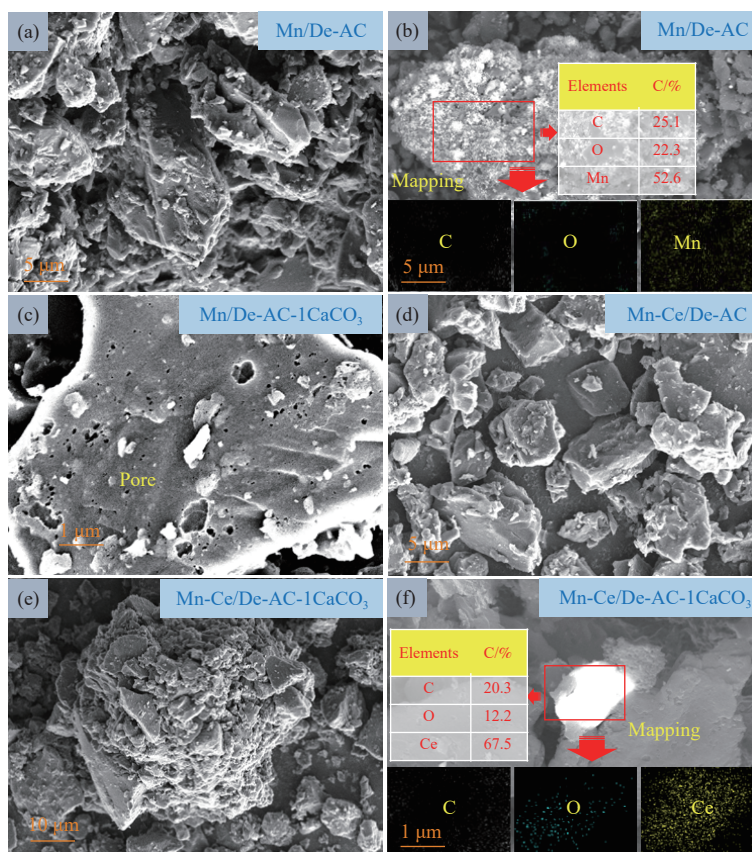


Fig. 5 SEM images of Mn/De-AC- $x\text{CaCO}_3$ and Mn-Ce/De-AC- $x\text{CaCO}_3$: Mn/De-AC (a) and (b), Mn/De-AC-1 CaCO_3 (c), Mn-Ce/De-AC (d), Mn-Ce/De-AC-1 CaCO_3 (e) and (f)

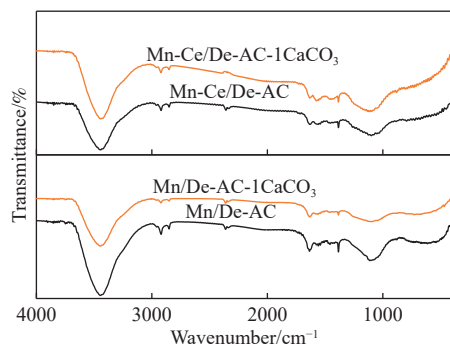


Fig. 6 FT-IR of Mn/De-AC- $x\text{CaCO}_3$ and Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts

The three peaks proposed to be synthesized for Mn 2*p* are shown in Figure 7(b), which are attributed to Mn^{4+} , Mn^{3+} , and Mn^{2+} , at the positions of 644.1 ± 0.1 , 641.9 ± 0.1 and 640.4 ± 0.1 eV, respectively^[21–22]. The eight peaks fitted to the Ce 3*d* separable peaks are shown in Figure 7(c), attributed to Ce^{4+} (916.6 ± 0.1 , 906.6 ± 0.1 , 900.7 ± 0.1 , 898.1 ± 0.1 , 888.1 ± 0.1 and 888.5 ± 0.1 eV) and Ce^{3+} (902.0 ± 0.1 and 884.7 ± 0.1 eV), respectively^[22]. Four peaks fitted to the O 1*s* are shown in Figure 7(d), which splitting at 530.2 ± 0.1 eV for lattice oxygen (O_β), at 531.8 ± 0.1 eV

for chemisorbed oxygen (O_α), at 533.3 ± 0.1 eV for oxygen in hydroxyls and carbonates (O_γ) and at 534.3 ± 0.1 eV for oxygen species in bound water (O_δ)^[23]. The content of the relevant valence states can be calculated from the ratio of peak areas corresponding to the elements in different valence states in Figure 7 (Table 2).

As shown in Table 2, the surface of SCR catalysts prepared based on AC structure regulated by calcite in coal contained higher contents of Mn^{4+} (21.4%), Mn^{3+} (45.7%), Ce^{4+} (28.8%) and chemisorbed oxygen (O_α , 43.3%), namely the surface of the Mn-Ce/De-1CaCO₃ catalysts had richer MnO₂ and CeO₂ substances, and thus the SCR catalyst has stronger surface oxidizable, which could accelerate the oxidation of NO and ultimately promote the SCR reaction (Equation (3)–(4)). The increase of Mn₂O₃ and CeO₂ substances on the surface of the SCR catalyst is one of the reasons for enhanced denitrification activity.

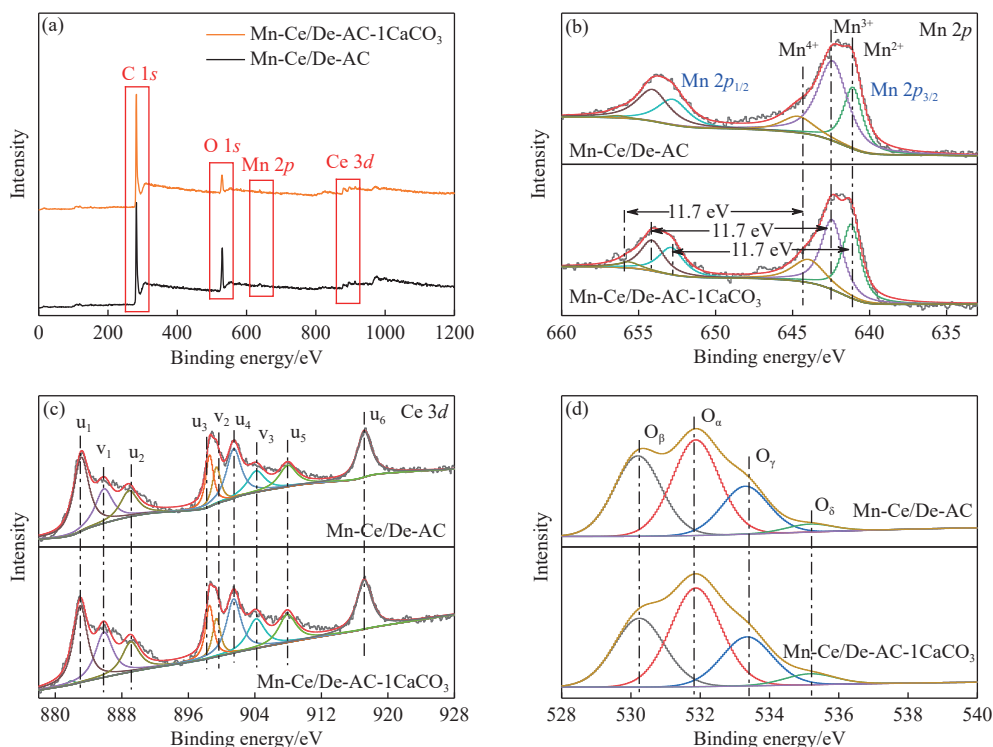
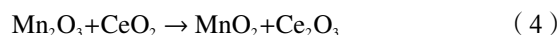


Fig. 7 The spectra of XPS survey spectra (a), Mn 2*p* (b), Ce 3*d* (c) and O 1*s* (d) of Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts

Table 2 Surface manganese, cerium and oxygen of Mn-Ce/De-AC- $x\text{CaCO}_3$ catalysts (%)

Sample	Mn^{4+}	Mn^{3+}	Mn^{2+}	Ce^{4+}	Ce^{3+}	O_β	O_α	O_γ	O_δ
Mn-Ce/De-AC	20.6	41.8	37.6	26.4	73.6	34.5	41.6	20.1	3.8
Mn-Ce/De-AC-1CaCO ₃	21.4	45.7	32.9	28.8	71.2	30.3	43.4	21.6	4.8

2.6 $\text{NO}+\text{O}_2$ -TPD

The adsorption and oxidation of NO are core aspects of the SCR reaction. To clarify the effect of SCR catalysts prepared by AC structure regulated by calcite in coal on NO adsorption and oxidation, $\text{NO}+\text{O}_2$ -TPD was performed (Figure 8). Analyses results showed that SCR catalysts exhibited clear NO_x desorption peaks (50–400 °C); among which the Mn-Ce/De-AC-1CaCO₃ catalyst had higher NO and NO₂ adsorption, reaching 0.181 and 0.036 mmol/g, respectively, which is significantly higher than that of the Mn-Ce/De-AC catalyst of 0.159 and 0.029 mmol/g. The increase in NO adsorption and oxidation by the Mn-Ce/De-AC-1CaCO₃ catalyst was mainly attributed to the calcite is favorable for the formation of oxygen-containing functional groups (such as C=O) of AC, which facilitates the dispersion of Mn-Ce. Meanwhile, abundant Mn₂O₃ and CeO₂ substances of the SCR catalyst favored the oxidation of NO. Overall, the Mn-Ce/De-AC-1CaCO₃ catalyst showed a higher NO and NO₂ adsorption capacity.

2.7 *In situ* DRIFTS analysis

To explore the reasons for higher denitration activity of SCR catalyst by AC structure regulated by calcite in coal, *in situ* DRIFTS analyses of Mn-Ce/De-AC-1CaCO₃ catalyst were conducted, and the results are shown in Figure 9.

DRIFT spectra of the Mn-Ce/De-AC-1CaCO₃ catalyst during the adsorption of NH₃ are shown in Figures 9(a) and (b). The absorption peaks appearing between 1000 and 1200 cm⁻¹ are typical peaks of Lewis acidic sites^[24]. The absorption peaks at wavenumbers 1418, 1456, 1523 and 1683 cm⁻¹ are caused by the symmetric bending vibration of NH₄⁺ in Brønsted acidic sites^[25]. The absorption peaks at wavenumbers 1455 and 1523 cm⁻¹ are caused by the N–H vibration of adsorbed ammonia^[26]. The absorption peak at wavenumbers 1683 cm⁻¹ is attributed to the formation of coordinated NH₃ at Lewis acidic sites.

The DRIFT spectra of the Mn-Ce/De-AC-1CaCO₃ catalyst after switching the introduced atmosphere from NH₃ to a mixture of NO and O₂ are shown in Figures 9(c) and (d). The stretching vibration at a wavenumber of 1317 cm⁻¹ is the stretching vibration peak of monodentate nitrate^[27]; the stretching vibrations at wavenumbers of 1804

and 1584 cm⁻¹ are caused by the stretching vibrations of bidentate nitrate^[28]; the stretching vibration at a wavenumber of 1485 cm⁻¹ is caused by the stretching vibration of nitrite^[28].

Figures 9(e) and (f) show the DRIFT spectra of the Mn-Ce/De-AC-1CaCO₃ catalyst under SCR atmosphere. The Mn-Ce/De-AC-1CaCO₃ catalyst exhibits NH₃ species at wavenumbers of 1000–1200, 1600 and 1685 cm⁻¹. Under the SCR stable reaction atmosphere, the absorption peak of bridged nitrates is at wavenumber 1220 cm⁻¹, the absorption peak of monodentate nitrates is at wavenumber 1317 cm⁻¹, and absorption peaks of bidentate nitrates are at wavenumber 1418 and 1583 cm⁻¹. AC structure regulated by calcite in coal facilitates the formation of abundant NH₃ activating species on the catalyst surface, which is beneficial for the formation of bidentate nitrates, promoting the SCR reaction, and enhancing denitrification activity.

2.8 Mechanism of enhancing the NH_3 -SCR performance of catalysts by the AC structure regulated by calcite in coal

Based on above analyses and discussions, the enhanced effect of the AC structure regulated by calcite in coal on the performance of the SCR catalyst was obtained (Figure 10). During the AC preparation process, calcite in coal enhanced activation of water vapor and carbon dioxide, which facilitated the formation of abundant oxygen-containing functional groups including C=O^[12], and finally facilitated the dispersion of Mn-Ce during SCR catalyst preparation process. The AC structure regulated by calcite in coal promoted the formation of MnO₂ and CeO₂ substances in SCR catalysts, which facilitated the generation of more chemisorbed oxygen, thus accelerating L-H reaction. The AC structure regulated by calcite in coal enabled more acidic sites in the SCR catalysts, which facilitated the adsorption of NO and NO₂. Overall, the AC structure regulated by calcite in coal improved the physicochemical properties of the SCR catalysts (higher Mn⁴⁺ and Ce⁴⁺/Ce³⁺, an abundance of chemisorbed oxygen, and acidic sites), which could strengthen the SCR reaction pathways (richer NH₃ activated species and bidentate nitrate active species), and therefore, denitrification performance enhanced.

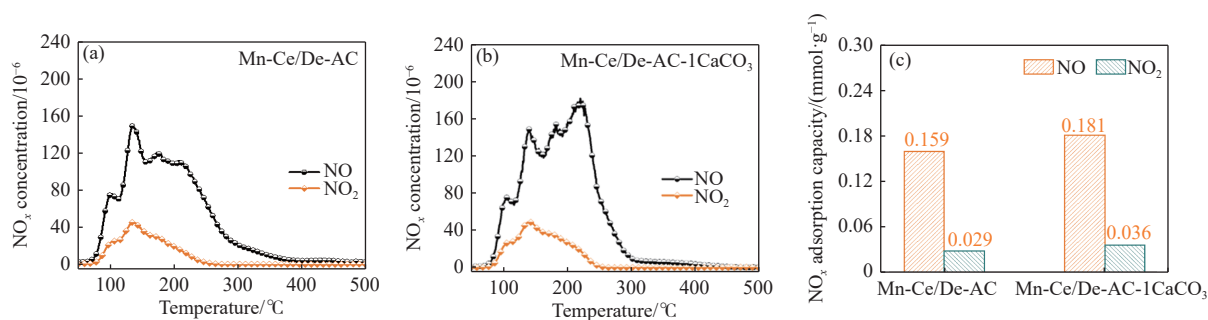


Fig. 8 $\text{NO}+\text{O}_2$ -TPD profiles of Mn-Ce/De-AC- x CaCO₃ catalysts

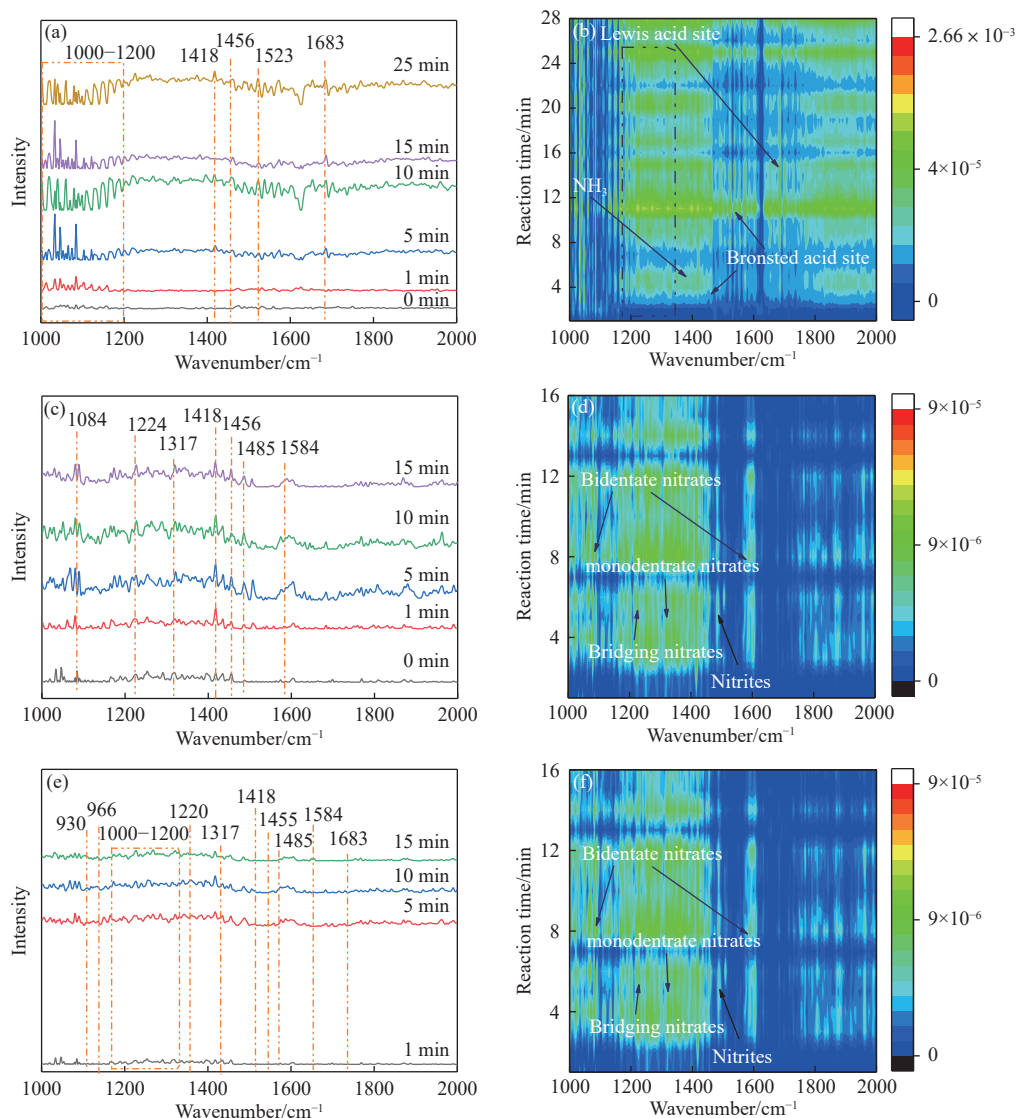


Fig. 9 *In situ* DRIFTS spectra of Mn-Ce/De-AC-1CaCO₃ catalyst at 120 °C during a single experiment where the sample is sequentially exposed to different gas mixtures: NH_3 adsorption (a) and (b), $\text{NO}+\text{O}_2$ (c) and (d), SCR atmosphere (e) and (f)

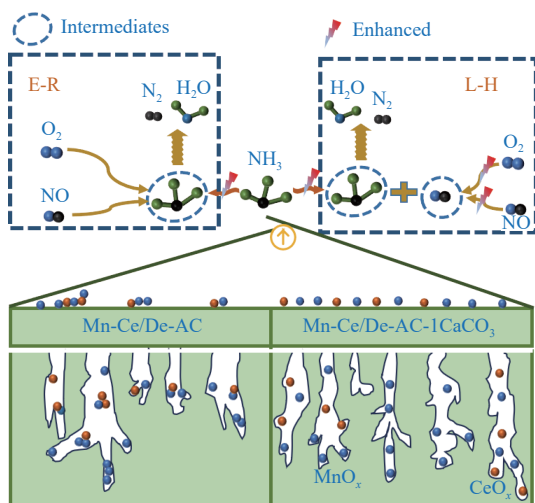


Fig. 10 The enhanced effect of the demineralized calcium-containing minerals activated carbon on the NH_3 -SCR performance of the catalyst

3 Conclusions

This study systematically investigated the enhancement mechanism of the AC structure regulated by calcite in coal on low-temperature denitrification performance of SCR catalysts after acid-washing method to remove calcium-containing minerals in AC. Experimental results showed that the AC structure regulated by calcite in coal enhanced denitrification activity of SCR catalysts. NO conversion increased from 88.3% for Mn-Ce/De-AC to 91.7% for Mn-Ce/De-AC-1CaCO₃ at 210 °C. The improved SCR denitrification activity results from the modification of physicochemical properties including higher Mn^{4+} content and $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio, an abundance of chemisorbed oxygen and acidic sites, which could strengthen the SCR reaction pathways (richer NH_3 activated species and bidentate nitrate active species); therefore, NO removal is enhanced. The results of this work could provide critical theoretical support and technical guidance for utilizing high calcium coal to construct high-performance low-temperature SCR

catalysts.

Declaration of Competing Interest

The authors declare no conflict of interest.

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煤中方解石调控的活性炭结构对 Mn-Ce/AC 催化剂 NH_3 -SCR 性能的强化机制

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摘 要: 为了探究煤中方解石调控的活性炭结构对 SCR 催化剂低温脱硝性能的影响, 本研究采用酸洗的方法脱除了活性炭中的含钙矿物质, 采用等体积浸渍的方法制备得到 Mn-Ce/De-AC- $x\text{CaCO}_3$ (x 为煤中方解石的含量) 催化剂。通过系列表征及低温脱硝活性测试明确了煤中方解石调控的活性炭结构对 SCR 催化剂脱硝性能的影响。结果表明, 煤中方解石调控的活性炭结构强化了 SCR 催化剂的脱硝性能。当温度为 210 °C 时, SCR 催化剂的脱硝率由 Mn-Ce/De-AC 的 88.3% 提高至 Mn-Ce/De-AC-1 CaCO_3 的 91.7%。煤中方解石调控的活性炭结构使 SCR 催化剂的理化性能得到改善, 具有更高的 Mn^{4+} 和 $\text{Ce}^{4+}/\text{Ce}^{3+}$ 含量、更高的化学吸附氧和丰富的酸性位点, 进而在脱硝反应中强化了 SCR 反应路径(丰富的 NH_3 活化物质和双齿硝酸盐活性物质等), 低温脱硝活性提高。

关键词: 方解石; 活性炭; 结构; Mn-Ce/AC 催化剂; NH_3 -SCR 性能

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