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Lu Yao (Conceptualization)
(Methodology) <ce:contributor-role>Writing - Original draft
(Investigation) (Formal analysis), Qingcai Liu (Supervision)
(Methodology) (Resources) (Funding acquisition), Susanne Mossin
(Methodology) (Resources) (Writing - review and editing), David
Nielsen (Investigation) (Visualization), Ming Kong (Validation)
(Writing - review and editing), Lijun Jiang (Investigation) (Formal
analysis) (Validation), Jie Yang (Investigation) (Formal analysis)
(Writing - review and editing), Shan Ren (Conceptualization)
(Funding acquisition) (Project administration), Juan Wen
(Resources) (Investigation) (Writing - review and editing)

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Promotional effects of nitrogen doping on catalytic performance over manganese-containing semi-coke catalysts for the NH₃-SCR at low temperatures

Lu Yao ^{a, b}, Qingcai Liu ^{a, *}, Susanne Mossin ^{b, *}, David Nielsen ^b, Ming Kong ^{a, b}, Lijun Jiang ^a, Jie Yang ^a, Shan Ren ^{a, *}, Juan Wen ^{a, c}

^a College of Materials Science and Engineering, Chongqing University, Chongqing, 400044, China

^b Department of Chemistry, Technical University of Denmark, Lyngby, 2800, Denmark

^c Chongqing Cheng Tou Road and Bridge Administration Co. Ltd, Chongqing, 400060, China

* corresponding author email: liu_qingcai@163.com (Qingcai Liu)

slmo@kemi.dtu.dk (Susanne Mossin)

shan.ren@cqu.edu.cn (Shan Ren)

Graphical Abstract

Highlights

- Nitrogen doping results in the appearance of pyridinic-N, pyrrolic-N and quaternary-N over the semi-coke catalyst.
- Nitrogen doping enhances the electron donor effect and electron mobility of the catalyst to improve the adsorption of NO.
- The intermediates formed by N-doping promote coordinated NH_3 and $-\text{NH}_2$ species to further participate in LT SCR reaction.
- ASC-10U10Mn catalyst exhibits the best catalytic performance for LT NH_3 -SCR reaction.

Abstract

A series of nitrogen-doped MnO_x /semi-coke catalysts were studied for low-temperature (LT) de- NO_x performance in the NH_3 -SCR reaction. Changes in morphology, structure, and surface chemistry of the semi-coke catalysts were systematically investigated to analyze the promotional effects of nitrogen doping on catalytic performance. The catalytic activity of ASC-10U10Mn was found to be enhanced significantly in a broad temperature range of 100–300°C, improving 44.2% at 150°C—the largest jump in this temperature range—and reaching 94.5% at 275°C. Nitrogen doping results in aromatic pyridinic-N, pyrrolic-N, and quaternary-N; the unpaired electrons on these groups play a critical role in enhancing the adsorption and oxidation of NO. NH_3 adsorption is enhanced due to numerous diverse Lewis acid sites on ASC-10U10Mn. The electron distribution of MnO_x /semi-coke catalysts and the electron mobility between manganese and oxygen species are improved by nitrogen doping. The resulting nitrate intermediates, especially bridging nitrates, can be reduced by NH_3 species at low temperatures. The increase in the number of oxygen vacancies improves oxidation of coordinated NH_3 . In addition, DRIFTS results suggest that coordinated NH_3 and intermediate $-\text{NH}_2$ are much more active and make a considerable positive contribution to the LT SCR reaction.

Key words

Nitrogen doping; MnO_x /semi-coke catalyst; Low-temperature SCR; Surface chemistry; Promotional mechanism

1. Introduction

Selective catalytic reduction (SCR) with ammonia is an effective technology to control nitrogen oxide pollution from stationary sources and a key part of this technology is the catalyst (Lu et al., 2018). Metallurgical industry is the second largest stationary emission source of nitrogen oxides after thermal power plants. Nevertheless, traditional $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ catalysts are not applicable for de- NO_x of the low-temperature (usually below 300°C) flue gas in the metallurgical industry, since catalysts have the optimum temperature range of $300\text{-}400^\circ\text{C}$. In addition, the toxicity and high price of $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ catalysts limit the application in other industrial fields (Fan et al., 2014; Li et al., 2017). Therefore, there is a high demand for an economical and eco-friendly catalyst system for de- NO_x at low temperatures.

The structural features and surface chemistry of catalyst support are important in new catalyst development, and they can affect the activity and stability of catalysts. Various carbon materials, such as activated carbon, activated carbon fibers, and activated coke/semi-coke, have drawn the researchers' attention for de- NO_x catalysis due to their low operating temperatures, regeneration capacity, and simplicity of modification (Shirahama et al., 2002; Zhu et al., 2000; Wang et al., 2014a; Jiang et al., 2019). As a byproduct of the metallurgical industry, semi-coke is both relatively inexpensive and accessible. From a material life-cycle perspective, it is also highly attractive to use semi-coke for catalyst preparation and thus integrate the recycling of solid

waste with atmospheric pollution control (Knoblauch et al., 1981; Wang et al., 2017). Some researchers (Lu et al., 2018; Wang et al., 2014a; Ren et al., 2017) have verified that semi-coke is a promising catalyst support for NH_3 -SCR due to its superior de- NO_x performance. However, it remains challenging to further improve de- NO_x activity at low temperatures (100–300°C).

In order to apply semi-coke to the large-scale treatment of LT flue gas, its surface chemistry must be modified in order to satisfy the conceived requirements of the catalytic reaction. One efficient modification method is to increase active sites by loading metal oxides, such as iron, cobalt, cerium, manganese, and lanthanum (Wang et al., 2017; Zhang et al., 2018; Yan et al., 2017). MnO_x catalysts exhibit excellent LT activity, but the differences in optimal performance among various catalysts, such as $\text{MnO}_x/\text{TiO}_2$, $\text{MnO}_x/\text{Al}_2\text{O}_3$ or MnO_x /carbon nanotubes, are also noticeable (Fang et al., 2015; Yang et al., 2020; Wang et al., 2014c). Another modification method to improve catalytic activity is to introduce surface functionalities (Klinik et al., 2011). The intrinsic properties and concentrations of functional groups are important for catalyst performance. Nitrogen functional groups are particularly intriguing (Figueiredo et al., 2007). Watanabe et al. (Watanabe et al., 2015) discovered through theoretical investigations that nitrogen doping contributes to the interaction between carbon atoms at the edges of graphite and oxygen functional groups. Some researchers (Liang et al., 2018; He et al., 2016) revealed that doping nitrogen into sp^2 -hybridized carbon frameworks could alter the nature of carbon materials to enhance catalytic activity. Nitrogen doping is widely used in catalyst modification to improve the activity of catalytic oxidation, photocatalytic reactions and catalytic decomposition processes (Sousa et al., 2012; Zhao et al., 2017; Wang et al., 2018), but thus far there have been only a few studies on the nitrogen doping of NH_3 -SCR catalysts.

Most research describes materials that have been modified in only one way, yet a few studies in the literature report combinations of the aforementioned methods on semi-coke to promote catalytic performance for LT NH_3 -SCR reaction. Grzybek et al. (Grzybek et al., 2008) attempted to prepare activated carbon catalysts using combined modification methods, although further mechanisms were not reported. A semi-coke catalyst modified with melamine and MnO_x was prepared, and the improved SCR activity indicated a bright future for combined modification methods (Yao et al., 2019). Nonetheless, the role of nitrogen functional groups and the promotional mechanisms of nitrogen doping on the catalytic performance of MnO_x /semi-coke catalysts remain undefined.

In this work, a series of nitrogen-doped MnO_x /semi-coke catalysts were prepared and investigated for the LT NH_3 -SCR performance. The physicochemical properties of the catalyst were systematically characterized by BET, SEM, XRD, XPS, NH_3 -TPD, H_2 -TPR and *in situ* DRIFTS in order to determine the promotional effects of nitrogen doping on the catalytic performance and demonstrate the possible reaction path during the LT NH_3 -SCR process.

2. Experiments

2.1 Catalyst preparation

Raw semi-coke in this work was obtained from Fugu, Shaanxi, China and its basic components are shown in Table 1. Before catalyst preparation, raw semi-coke was crushed and sieved into particles ranging 20-40 mesh and then pretreated in nitric acid solution (60 wt.%) at 80°C for 3 h. The pretreated semi-coke was washed with distilled water until washing water remained neutral and then dried fully at 100°C. Activated semi-coke was obtained and marked

as ASC.

Table 1

Proximate and elemental analysis results of semi-coke.

Sample	Proximate analysis (%)				Elemental analysis (%)				
	Moisture	Ash	Volatile	Fix carbon	C	H	O	N	S
Semi-coke	0.21	10.46	8.67	80.66	88.23	1.37	7.05	1.88	1.04

A series of nitrogen-doped MnO_x /semi-coke catalysts were prepared by impregnation with a mixture of urea and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. The preparation process consisted of the following steps: (1) dissolving different relative amounts of urea and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in distilled water while stirring; (2) adding ASC to above solution and sonicating for 30 min, then continuing the stirring for 3 h; (3) drying the samples at 100°C for 12 h; (4) calcining the samples in N_2 with a ramp of $2^\circ\text{C}/\text{min}$ to 400°C and maintaining 6 h; and (5) cooling the calcined samples to room temperature in a N_2 atmosphere. Nitrogen-doped MnO_x /semi-coke catalysts were thus obtained and denoted as ASC- $x\text{UyMn}$, in which x and y represent the mass loading amounts of urea and MnO_x , respectively. The content of major elements in the semi-coke catalysts was detected by ICP-OES (PerkinElmer Optima 8000) and elemental analysis, and the results are listed in Table 3 and Table 4.

2.2 Catalytic performance measurements

SCR activity measurements were carried out at atmospheric pressure in a fixed-bed quartz reactor of 10 mm inner diameter with 1 g catalyst under the following simulated reactant gas conditions: 0.05% NO , 0.05% NH_3 , 5% O_2 , 0.01% SO_2 (when used), and 5% H_2O (when used) with N_2 balance gas at a total flow of 500 mL/min, and GHSV 16000 h^{-1} . The outlet

concentrations of NO and NO₂ were detected by an MRU OPTIMA7 (Germany) gas analyzer, and N₂O was detected by a SinGoAn SGA-500B (China) N₂O detector. The NO conversion and N₂ selectivity were calculated using the following equations:

$$\text{NO conversion}(\%) = \frac{NO_{in} - NO_{out}}{NO_{in}} \times 100\%$$

$$N_2 \text{ selectivity}(\%) = \left(1 - \frac{2N_2O_{out} + NO_{2out}}{NO_{in} + NH_{3in}}\right) \times 100\%$$

Where the subscripts *in* and *out* represented the inlet and outlet concentration which were gathered after attaining steady state, respectively.

2.3 Physical and chemical characterization

Scanning electron microscope (SEM) analysis was conducted on a VEGA3 TESCAN with an accelerating voltage of 20 kV. Energy dispersive X-ray spectrometry (EDS) mapping was recorded to determine the content and distribution of elements. BET surface area of the samples was determined from N₂ physisorption measurements on about 100 mg sample at 77 K with a Micromeritics ASAP 2010 instrument. The sample was heated to 200°C for 1 h prior to the measurement.

X-ray diffraction (XRD) were performed on a Rigaku D/max-2500 powder diffractometer using Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) at 40 kV and 40 mA over the range of $10^\circ \leq 2\theta \leq 90^\circ$. Crystalline phases were identified by comparison with the reference data from JCPDs.

X-ray photoelectron spectroscopy (XPS) were measured on a Thermo scientific system (ESCALAB 250Xi) at room temperature using Al K α radiation (1484.6 eV). Before acquisition of data, the sample was outgassed for 1 h in vacuum to minimize surface contamination. The spectra were deconvoluted using Avantage Data system software.

NH₃ temperature-programmed desorption (NH₃-TPD) were conducted on a Micromeritics Autochem-II instrument. In each typical measurement, 150 mg of dried sample was placed in a U-shaped quartz tube and pretreated in 50 mL/min He from room temperature to 300°C then cooled to 60°C. The sample was then exposed to dry NH₃ gas (5% NH₃ in He) for 1 h. After NH₃ adsorption, the sample was flushed with He for 1 h at 60°C. The TPD operation was conducted in 50 mL/min He from 60 to 700°C (10°C/min).

H₂ temperature-programmed reduction (H₂-TPR) measurements were conducted on a Micromeritics Autochem-II instrument. In each typical measurement, 200 mg of dried sample was placed in a U-shaped quartz tube and pretreated in 50 mL/min He from room temperature to 200°C for 1 h and cooled to 60°C. H₂-TPR analysis was carried out in a reducing mixture (50 mL/min) consisting of 5% H₂ and balance Ar from 60 to 700°C (10°C/min). The H₂ concentration in the effluent stream was monitored by a thermal conductivity detector (TCD).

In situ diffuse reflectance infrared Fourier transform spectra (*in situ* DRIFTS) were collected from 700 to 4000 cm⁻¹ by accumulating 64 scans with at a spectral resolution of 8 cm⁻¹ on a Nicolet iS50 FTIR spectrometer equipped with an MCT detector cooled by liquid N₂. Before each experiment, the sample was pretreated at 250°C for 2 h in 200 mL/min He and cooled to 200°C. The background spectrum was collected in flowing He and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: 0.12% NH₃, 0.12% NO, 5% O₂ with He balance gas at a total flow of 200 mL/min.

3. Results and discussion

3.1 Catalytic performance

Fig. 1(a) shows the de-NO_x performance of semi-coke catalysts with different N-doping amount as a function of reaction temperature. ASC exhibited steady-state NO conversion of approximately 10% over the entire temperature range. Nitrogen-doped semi-coke catalysts displayed a sharp decrease followed by a moderate increase in NO conversion. A similar trend of NO conversion was also observed by Grzybek et al. (Grzybek et al., 2008) for nitrogen-doped active carbon. ASC-5U exhibited the lowest NO conversion of 14.2% at 150°C, for which increased nitrogen-doping induced a further decrease in NO conversion. Moreover, the conversion gaps among all the nitrogen-doped catalysts visibly increased above 175°C.

Fig. 1(b) shows the de-NO_x performance of nitrogen-doped MnO_x/semi-coke catalysts as a function of reaction temperature. Loading MnO_x does indeed improve the NO conversion of the catalyst, as mentioned in the Introduction. Furthermore, after the nitrogen-doping of MnO_x/semi-coke catalysts, the NH₃-SCR performance improves markedly in the range 100–200°C, especially at 150°C, at which the increase of NO conversion achieved its maximum value of 44.2%. The NO conversion was 48.3% for ASC-5U10Mn (blue in Fig. 1) and increased to 63.5% for ASC-10U10Mn (pink) at 125 °C. With the increase of N-doping, the NO conversion decreased to 59.8% for ASC-15U10Mn (orange). For ASC-10Mn (green), the NO conversion could only reach the same level when the reaction temperature was above 200°C. ASC-10U10Mn exhibited the optimum NO conversion of 94.5% at 275°C and was effective in a broad temperature range of 100–300°C. Specially, the NO conversion of ASC-15U10Mn was

no longer increased with higher N-doping amount, which was close to that of ASC-10U10Mn below 200°C. The NO conversion of ASC-15U10Mn, however, was obviously lower than that of ASC-10U10Mn as the reaction temperature was above 225°C. And the conversion gap between nitrogen-doped MnO_x /semi-coke catalysts and ASC-10Mn diminishes within this reaction temperature range. Some researchers (Wang et al., 2012; Sun et al., 2017) also reported a similar trend above 250°C for MnO_x /MWCNTs catalysts and bulk MnO_x catalysts.

The N_2 selectivity of semi-coke catalysts were also measured and shown in Fig. S1. The N_2 selectivity increased obviously under 175 °C with N-doping amount. Moreover, the N_2 selectivity of ASC-10U10Mn could reach above 95% when the temperature was below 150°C. Both of the improved NO conversion and N_2 selectivity of ASC-10U10Mn demonstrated that N-doping could promote catalytic performance of ASC-10U10Mn.

Fig.1 De-NO_x activity of (a) semi-coke catalysts with different N-doping amount; (b) nitrogen doped MnO_x/semi-coke catalysts; (c) ASC-10Mn and ASC-10U10Mn in the presence of SO₂ at 225°C; (d) ASC-10Mn and ASC-10U10Mn in the presence of SO₂+H₂O at 225°C.

After the flue gas purification process of metallurgical industry, there is still a trace amount of SO₂ (approximately 100 ppm) and H₂O (approximately 5 vol%). Therefore, the influences of SO₂ and H₂O on the de-NO_x activity of ASC-10Mn and ASC-10U10Mn were investigated, as shown in Fig. 1(c) and 1(d). Both ASC-10Mn and ASC-10U10Mn exhibited high NO conversion in the absence of SO₂, although the NO conversion of ASC-10U10Mn was higher than that of ASC-10Mn. After introducing SO₂, the NO conversion of ASC-10Mn decreased by approximately 17% from 77.6% in 180 min, and the NO conversion of ASC-10U10Mn dropped by approximately 14% from 90.0% in 200 min. When SO₂ was removed, ASC-10Mn and ASC-10U10Mn barely recovered. After the simultaneous introduction of SO₂ and H₂O, the deactivation of ASC-10Mn and ASC-10U10Mn was faster and more significant than those in the presence of SO₂, indicating that the poisoning effects of SO₂ and H₂O on de-NO_x performance of semi-coke catalysts were stronger. Also, the inhibition effects of SO₂ and H₂O were irreversible.

3.2 Characterization of the catalysts

3.2.1 Morphology

SEM images revealed the extent of modification on semi-coke catalysts. As seen in Fig. 2, the surface of the raw semi-coke was relatively smooth, with no obviously developed pores.

After pretreatment in nitric acid solution, the surface of the ASC was completely different from that of the raw semi-coke. Variably sized pores and laminar structures with ditches can be readily distinguished on ASC. These morphological changes are the result of nitric acid consuming volatile components in the semi-coke, thereby opening closed pores. A similar phenomenon has been noted in the literature for other carbon material-based catalysts (Su et al., 2013; Chuang et al., 2011). The development of a porous structure provides more binding points between the support and MnO_x or doped nitrogen, indicating the necessity of pretreating the semi-coke with nitric acid.

Fig. 2 SEM images of semi-coke catalysts and the corresponding elemental mapping by EDS

Compared with ASC, ASC-10Mn exhibited a much denser laminar structure and a mass of fine particles dispersed evenly in the ditches. This agrees with the EDS image of ASC-10Mn, which revealed the density of Mn to be sparse and even. ASC-10U exhibited a large number of

net-like pores with much clearer flaky shapes. The density of nitrogen was scattered and indistinct in the EDS mapping of ASC-10U. Hence, it is difficult to estimate whether the morphology effects derived entirely from nitrogen doping. Notably, the morphology of ASC-10U10Mn was completely different from that of other catalysts, retaining some net-like pores and presenting a distinct laminar structure. Although the manganese content of ASC-10U10Mn was almost the same as that of ASC-10Mn, as proved in Table 4, the Mn density was significantly higher at the corresponding positions of the ESD images, where the laminar structures were located. The distribution of nitrogen was more homogeneous and the density was higher on ASC-10U10Mn than on ASC-10U.

3.2.2 Structural properties

XRD measurements were conducted in order to study the crystallinity and dispersion of active phases on the catalysts. Fig. 3 compares the XRD patterns of manganese-containing catalyst samples to ASC before and after catalytic testing. There were 2 typical broad peaks at 24.6° and 43.4° in the XRD patterns of all the samples, which were both assigned to amorphous carbon (Gao et al., 2011; Prahas et al., 2008). The intensity of these peaks remained unchanged, suggesting that the carbon structure was undamaged. For ASC, weak diffraction peaks were observed at 20.8° , 26.6° , 36.5° , 39.4° , 50.0° , 59.9° , and 68.4° . These were assigned to low SiO_2 content in the ash of the semi-coke (Lu et al., 2018; Gao et al., 2011). Since SiO_2 was unchanged during the modification and de- NO_x catalysis process, the SiO_2 diffraction peaks were present in the XRD patterns of all samples.

For fresh catalysts, peaks assigned to MnO_2 at 35.1° and 58.9° ; Mn_3O_4 at 36.1° and 60° ; and

MnO at 40.7° , 70.4° , and 73.9° were found in all the XRD patterns (Fig. 3 and Fig.S2) (Wang et al., 2012; You et al., 2017; Wang et al., 2014d; Yang et al., 2017), demonstrating that MnO_x were successfully loaded on all the catalysts. An additional peak at 32.6° in the patterns for ASC-5U10Mn and ASC-10U10Mn corresponded to Mn_3O_4 . There was no obvious difference between the XRD patterns of ASC-5U10Mn and ASC-10U10Mn. Previous works (Fang et al., 2013; Kang et al., 2007) reported that a higher valence state of Mn was preferable for the redox property of MnO_x /catalysts in LT SCR reactions and MnO exhibited the poorest SCR activity among MnO_x . This may explain the enhanced LT SCR activity of nitrogen-doped MnO_x /semi-coke catalysts. In addition, structural defects induced by N-doping possibly facilitate the transition between Mn_3O_4 and MnO_2 , which provides more active oxygen sites.

Fig.3 XRD patterns of semi-coke catalysts: (a) ASC, (b) ASC-10Mn, (c) ASC-10Mn-after, (d) ASC-10U10Mn, (e) ASC-10U10Mn-after

On the spent catalyst ASC-10Mn-after, the MnO peak was only observed at 40.7° as shown in Fig. 3. The intensity of MnO peak changed obviously and the peak became invisible

compared with the fresh catalysts. This suggests decreased crystal particle size and crystallinity degree of MnO. All the peaks ascribed to MnO_2 had disappeared. In ASC-10U10Mn-after, only the Mn_3O_4 peaks were observed. Based on the above comparisons of catalytic activity, the appearance of Mn_3O_4 had no negative impacts on the catalytic activity while MnO_2 was consumed. Wang et al. (Wang et al., 2012) also observed that Mn_3O_4 had the same effect on other carbon-based catalysts. Additionally, there was no distinct diffraction peak assigned to MnO on ASC-10U10Mn-after, illustrating that MnO could become more dispersed during the SCR reaction.

3.2.3 BET surface areas and pore size distributions

Fig. 4 shows the nitrogen adsorption-desorption isotherms and pore size distributions of ASC, ASC-10Mn, ASC5U10Mn (Fig. S3) and ASC-10U10Mn. There are clear differences between the adsorption and desorption branches in the isotherms of all the catalysts. All the catalysts exhibit type IV isotherms with a type H4 hysteresis, indicating that the micropores, mesopores, and slit-pore structures present in semi-coke catalysts are in strong accordance with the SEM results. The pore distribution plots suggest that most pores are 3–4 nm, implying that semi-coke catalysts are typical mesoporous materials.

Fig.4 N₂ adsorption-desorption isotherms and pore distribution plots of semi-coke catalysts**Table 2**

BET surface area and pore parameters of semi-coke catalysts.

Sample	BET surface area /m ² ·g ⁻¹	Average pore width /nm	Total pore volume /cm ³ ·g ⁻¹
ASC	79.2	6.0	0.044
ASC-10Mn	58.4	13.0	0.037
ASC-10U10Mn	38.0	8.2	0.026

The data in Table 2 and Table S1 reveal significant differences in the BET surface area and pore parameters of ASC and semi-coke catalysts. Compared with ASC, semi-coke catalysts exhibit smaller BET surface area and total pore volume, and bigger average pore width. As manganese or nitrogen inserted into the pores or interlayers of ASC during the impregnation or calcination process, some pores were blocked or even collapsed, causing the BET surface area and total pore volume to decrease, and the average pore width to increase (Gao et al., 2018; Ruiz et al., 2008). When Mn-loading amounts were the same for the catalysts, BET surface area, average pore width and total pore volume would decrease with the N-doping amount.

3.2.4 XPS characterization

XPS was used for investigating the identity and valence state of atoms on the surface of catalysts. The concentrations of oxygen, nitrogen, and manganese species were calculated and are summarized in Table 3 and Table 4. Figs. 5(a), (c), and (e) show the O 1s XPS spectra of ASC, ASC-10Mn, and ASC-10U10Mn, respectively. The O 1s spectra of all the samples could be fitted with 3 peaks, which were assigned to hydroxide groups (O_γ), surface chemical oxygen

(O_α), and crystal lattice oxygen (O_β). Loading manganese or nitrogen on catalysts did not affect the oxygen species, but did improve the O_α and O_β concentrations, which promoted oxygen mobility and oxygen vacancies (Gao et al., 2018). The highest O_γ concentration was found on ASC and was beneficial for NH_3 absorption as Brønsted sites, which was consistent with the NH_3 -TPD results. After loading manganese, the O_α concentration increased from 35.7% of ASC to 64.4% of ASC-10Mn which exhibited the apparent improvement of de- NO_x activity. The literatures reported that O_α could promote the oxidation of NO (Li et al., 2017; Jiang et al., 2019), suggesting that the improved catalytic activity of ASC-10Mn could cause by the increased O_α . With the nitrogen doping, the O_α concentration decreased, and the O_β and O_γ concentrations increased. The O_γ concentration of ASC-5U10Mn and ASC-10U10Mn was close (Fig. S4 and Table S2). There was the least O_α and the most O_β on the most active ASC-10U10Mn, but it exhibited the lowest O 1s binding energy among all catalysts, also indicating enhanced oxygen mobility (France et al., 2017). And the O_α concentration is not the dominate factor to affect the low-temperature catalytic activity of ASC-10U10Mn.

Table 3

Distribution of sites from surface XPS: Concentration of oxygen species is determined from the O 1s peak and nitrogen species from the N 1s peak. Number are given in %.

Sample	O ^a	O_α	O_β	O_γ	N ^a	N-6	N-5	N-Q	N-X	-NO ₂
ASC	8.0	35.7	13.5	50.8	1.3	57.7	-	-	2.3	40.0
ASC-10Mn	8.2	64.4	17.1	18.5	1.2	91.4	-	-	4.8	3.8
ASC-10U10Mn	8.5	37.0	37.7	25.4	4.8	33.6	32.6	18.7	-	15.2

^a Oxygen and nitrogen content obtained from elemental analysis

Fig.5 O 1s and N 1s XPS spectra of (a)(b) ASC, (c)(d) ASC-10Mn, (e)(f) ASC-10U10Mn

As shown in Figs. 5(b) and (d), the N 1s spectra of ASC and ASC-10Mn could be fitted with 3 peaks, assigned to pyridinic-N (N-6), oxidized pyridinic-N (N-X), and R-ONO (-NO₂) (Yao et al., 2019). The N-6 concentration was 57.7% on ASC and increased to 91.4% on ASC-10Mn. But the N-6 concentration gradually decreased and the new nitrogen species (quaternary-N, N-

Q) was induced with N-doping, as shown in Fig.S4 and Table S2. For ASC-10U10Mn, the N-6 concentration decreased sharply, and another new nitrogen species (pyrrolic-N, N-5) was induced (Yao et al., 2019; Shi et al., 2018). N-5 is mainly formed from the pyrolysis of any functional group containing NH_2 (Strelko et al., 2000), consistent with the high dosage of urea during the modification. N-6, N-5, and N-Q all have similar structures where nitrogen is doped in the aromatic rings. N-5 and N-6 are both electron pair donors. For N-6, its lone pair is not part of the aromatic π -system and is available for donation. N-5 is a much weaker Lewis base than N-6 since its lone pair is engaged in the aromatic π -system. N-Q has sp^2 hybridization and fully saturated bonding, which improves the electron mobility (Qiu et al., 2018). The electron distribution in catalysts was favorably affected by the addition of nitrogen functional groups.

Fig.6 Mn 2p XPS spectra of (a) ASC-10Mn, (b)ASC-10U10Mn

Table 4

Distribution of sites from surface XPS: Concentration of manganese species from the Mn 2p peak. Number are given in %.

Sample	Mn ^b	Mn ²⁺	Mn ³⁺	Mn ⁴⁺
ASC-10Mn	5.2	40.6	45.7	13.8
ASC-10U10Mn	5.3	30.1	44.8	25.1

^b Manganese content obtained from ICP-OES

The Mn 2p_{3/2} spectra of all the catalysts could be fitted with 3 peaks (Fig. 6 and Fig. S4), corresponding to Mn²⁺, Mn³⁺, and Mn⁴⁺, consistent with the XRD results. The relative concentrations of the different Mn species were calculated and are listed in Table 4 and Table S2. Mn³⁺ was the dominant form of manganese on semi-coke catalysts. Jia et al. (Jia et al., 2016) reported that when Mn³⁺ is present in the framework of MnO₂, oxygen vacancies can balance the charge as follows:

Where V_O is the oxygen vacancy site. For ASC-10Mn, more oxygen vacancies were present, therefore there was the higher O_a concentration (Table 3). Nevertheless, any peak assigned to Mn₂O₃ was not found in the corresponding XRD pattern, suggesting that Mn₂O₃ is the amorphous phase that is favorable for catalytic reduction (Zhang et al., 2016; Tang et al., 2007). Nitrogen doping has the least effect on the Mn³⁺ concentration and the more effect on the Mn²⁺ and Mn⁴⁺ concentrations. The Mn²⁺ and Mn³⁺ concentrations reduced and the Mn⁴⁺ concentration gradually increased with the N-doping amount. There was only 30.1% Mn²⁺ on ASC-10U10Mn, but the Mn⁴⁺ concentration was the highest: Mn⁴⁺/Mn³⁺ = 0.56. More active Mn⁴⁺ is beneficial to the oxidation of NO to NO₂ and the promotion of catalytic activity. More specific analysis is stated in the following discussion.

3.2.5 Redox performance

H₂-TPR was used for evaluating the reducibility of catalysts. The H₂-TPR profiles are shown

in Fig. 7. Gaussian fitting revealed that all the samples exhibited 4 overlapping reduction peaks. The 3 peaks in the range of 250–600°C derived from the 3 reduction steps: MnO_2 to Mn_2O_3 , Mn_2O_3 to Mn_3O_4 , and Mn_3O_4 to MnO . Another peak above 600°C was assigned to the reduction of oxygen functional groups on the surface of the matrix (Yan et al., 2017; Jiang et al., 2018).

Fig. 7 The H_2 -TPR profiles of (a) ASC-10Mn, (b) ASC-10Mn-after, (c) ASC-10U10Mn, (d) ASC-10U10Mn-after

Compared with ASC-10Mn, all reduction peaks of nitrogen-doped MnO_x /semi-coke catalysts gradually shifted to lower temperatures, indicating that nitrogen-doped MnO_x /semi-coke catalysts were more reducible than ASC-10Mn. Combined with the XRD and XPS results, the amorphous phase Mn_2O_3 can remain on nitrogen-doped MnO_x /semi-coke catalysts, which might be one reason for the high reducibility. As shown in Table 5 and Table S3, the area ratio of the MnO_2 to Mn_2O_3 reduction peak gradually increased with the N-doping amount, demonstrating more Mn^{4+} on ASC-10U10Mn. The largest MnO_x reduction peak of ASC-10U10Mn was attributed to the reduction of Mn_2O_3 to Mn_3O_4 , implying that Mn^{3+} is dominant.

The area ratio of the same reduction peak over ASC-10Mn was a little larger than that of ASC-10U10Mn, suggesting more Mn^{3+} over ASC-10Mn, in accordance with the XPS results. Furthermore, ASC-10U10Mn exhibited a larger reduction peak area for the oxygen functional groups on the semi-coke matrix, indicating that more oxygen functional groups were reduced. Nitrogen functional groups resulted in the increased reduction potential of oxygen species, making it possible to enhance the oxygen mobility of the catalysts. Accordingly, the reduction temperature of the oxygen species was reduced, implying that the oxygen species were easier to reduce, thus further promoting the redox property of ASC-10U10Mn.

Table 5

Relative area of reduction peaks of ASC10Mn and ASC10U10Mn before and after de- NO_x reaction determined from H_2 -TPR.

Sample	Area ratio of reduction peak/%			
	MnO_2 to Mn_2O_3	Mn_2O_3 to Mn_3O_4	Mn_3O_4 to MnO	Semi-coke matrix
ASC-10Mn	1.1	33.0	40.6	25.2
ASC-10Mn-after	1.8	50.6	31.9	15.7
ASC-10U10Mn	2.7	31.6	27.5	38.3
ASC-10U10Mn-after	8.9	34.2	38.8	18.2

All reduction peaks of the spent ASC-10Mn and ASC-10U10Mn shifted to higher temperature compared to the fresh catalysts, revealing that the reducibility of the active species had decreased. The area ratio of reduction peak of oxygen functional groups was reduced as well after reaction. This phenomenon indicates that oxygen functional groups are simultaneously involved in the SCR reaction.

3.2.6 Acidic performance

NH₃-TPD was used to estimate the surface acidity of catalysts. Fig. 8(a) and Fig. S6 show the NH₃-TPD patterns of the ASC, ASC-10Mn, ASC-5U10Mn, and ASC-10U10Mn catalysts. The surface acidity was calculated and is listed in Table 6 and Table S4. The TPD patterns of all the samples displayed a desorption peak around 114°C, which derived from the breakage of fairly weak hydrogen bonds between adsorbed NH₃ and surface acidic groups (Wang et al., 2015). ASC exhibited distinctive Brønsted acid and Lewis acid sites at 382°C and 605°C, respectively (You et al., 2017). For ASC-10Mn, the desorption peak assigned to the Brønsted acid sites shifted to a higher temperature, whereas the peak assigned to the Lewis acid sites remained unchanged, revealing that the addition of MnO_x led to the enhanced strength of the Brønsted acid sites. The decreased areas of all desorption peaks implied that ASC-10Mn could possess relatively few Brønsted acid and Lewis acid sites. The addition of MnO_x made it possible for some manganese to be present at the ion exchange sites, thereby reducing acid sites, something that was also observed in other catalysts (Sultana et al., 2012). The Brønsted and Lewis acid sites on catalysts were affected significantly by nitrogen doping. With the N-doping amount, the desorption peak attributed to the Brønsted acid sites gradually disappeared, and the strong peak attributed to the Lewis acid sites around 555°C gradually increased.

Fig.8 NH_3 -TPD profiles of semi-coke catalysts

Table 6

Surface acidity of semi-coke catalysts determined by NH_3 -TPD

Sample	Surface acidity/ $\text{mmol} \cdot \text{g}^{-1}$	
	Brønsted acid sites	Lewis acid sites
ASC	0.24	0.36
ASC-10Mn	0.10	0.27
ASC-10U10Mn	0.02	0.35

Gaussian fitting was employed to further explore the acid site changes, as shown in Fig. 8(b). The desorption peaks related to the Brønsted acid site in the range 250–440°C and the Lewis acid site above 450°C were broader for ASC-10Mn compared to ASC. These peaks required fitting with 2 Gaussian functions each, indicating the presence of multiple Brønsted and Lewis acid sites of different strengths. The desorption peaks of ASC-10U10Mn were fitted to only 1 Brønsted acid site and 4 different Lewis acid sites. After nitrogen doping, fewer Brønsted acid sites were present, but a greater diversity of species and more Lewis acid sites were present on ASC-10U10Mn. This is possibly a result of the retaining dispersion of active phases and the increased number of active sites after nitrogen doping.

3.2.7 *In situ* DRIFTS characterization

In situ DRIFTS was used to investigate the intermediates, the reaction pathway, and the possible reaction mechanisms of nitrogen-doped MnO_x/semi-coke catalysts at low temperatures. The formation of active sites, the transformation of adsorbed species, and the generation of intermediates over the ASC-10U10Mn catalyst were compared and analyzed based on the successive *in situ* DRIFT spectra recorded during different gas conditions. As illustrated in Fig. 9, *in situ* DRIFT spectra of ASC-10U10Mn were recorded at 200°C while exposed in sequence to NH₃, NO+O₂, and SCR atmospheres for 30 min.

Adsorption of NH₃. When ASC-10U10Mn was exposed to an NH₃ atmosphere, as shown in Fig. 9(a), clear changes were observed in the bands at 768, 930, 965, 1085, 1540, 1552, 1649, and 1685 cm⁻¹. The band at 768 cm⁻¹ appearing in all the spectra was assigned to Si-O. It has been ascertained by XRD that SiO₂ is always present on semi-coke catalysts (Lu et al., 2018). The noticeable bands at 930 and 965 cm⁻¹ appeared whenever the catalyst was exposed to NH₃. They were assigned to either gas phase or weakly adsorbed NH₃. The band at 930 cm⁻¹ exhibited slower change and lower intensity than the band at 965 cm⁻¹, although it gradually stabilized with time. The band at 1085 cm⁻¹ and the weak bands at 1624 cm⁻¹ represented the symmetric and asymmetric N-H bending vibrations of coordinated NH₃ on Lewis acid sites, respectively (Yan et al., 2017; Gao et al., 2017; Yu et al., 2017; Chen et al., 2015). The bands at 1649 and 1685 cm⁻¹ were attributed to the symmetric bending vibrations of NH₄⁺ species after reaction with Brønsted acid sites (Yu et al., 2017; Wang et al., 2014b). The changes of the weak bands at 1540 and 1552 cm⁻¹ were attributed to amide species (-NH₂) and intermediates from the partial oxidation of NH₃ (Yan et al., 2017; Chen et al., 2015). As explained in the literature (Yu

et al., 2017), -NH_2 species may arise from the partial oxidation of NH_3 caused by the abundant Mn^{3+} species on ASC-10U10Mn. The bands in the range of $1495\text{--}1510\text{ cm}^{-1}$ and $1560\text{--}1575\text{ cm}^{-1}$ due to pyridinic and pyrrolic structure, respectively, appeared and remained stable with time (Jia et al., 2002).

Fig. 9 *in situ* DRIFT spectra of semi-coke catalysts exposed to different atmospheres (a) Selected spectra of ASC-10U10Mn at 200°C during a single experiment where the sample is sequentially exposed to different gas mixtures, (b) Comparison of ASC-10Mn and ASC-10U10Mn at 200°C in NH_3 and in $\text{NO}+\text{O}_2$, (c) Comparison of the same sample and gas mixtures as in b) at different temperatures.

Co-adsorption of NO and O₂. When a mixture of NO and O₂ was introduced into the reaction chamber, the weak bands at 1124 and 1852 cm⁻¹ ascribed to either gas phase or weakly adsorbed NO appeared, and the gas phase or weakly adsorbed NH₃ associated with the bands at 965 and 930 cm⁻¹ disappeared immediately. As the chamber with the sample was being purged for 30 min, a new band at 1634 cm⁻¹ assigned to either gas phase or weakly adsorbed NO₂ appeared (Chen et al., 2015; Wang et al., 2014b). As time increased, the band at 1174 cm⁻¹ assigned to cis-N₂O₂²⁻ was observed (Yan et al., 2017; Chen et al., 2015), suggesting the improved oxidation of NO to NO₂. A band at 1191 cm⁻¹ assigned to anionic nitrosyl NO⁻ species was also detected (Gao et al., 2018; Qi et al., 2004). This species was expected to be oxidized to nitrate or nitrite in the presence of oxygen. Bridging nitrate at 1610 cm⁻¹, as well as the band at 1322 cm⁻¹ assigned to bidentate nitrate (Yu et al., 2017), appeared immediately after passing the NO+O₂ gas mixture for 5 min. The band at 1374 cm⁻¹ assigned to the free nitrate ion (-NO₃⁻) (Hadjiivanov et al., 2000) decreased upon exposure to NH₃, implying that free nitrate ions could adsorb NH₃ and possibly generate intermediates. When the gas turned to NO and O₂, the band at 1374 cm⁻¹ appeared again. Notably, the intensity of the bands assigned to the pyridinic and pyrrolic groups decreased over the 30 min exposure to NO and O₂. It can be speculated that N-doping contributed to the adsorption of NO and the further oxidation of NO. The intensity of the bands of any coordinated NH₃ and NH₄⁺ decreased at different degrees, implying that both coordinated NH₃ and NH₄⁺ species participate in the SCR reaction.

The spectra of ASC-10Mn and ASC-10U10Mn under the same atmosphere were compared in Fig. 9(b). In the case of NH₃, the bands at 1540, 1552, 1649, and 1685 cm⁻¹ could be observed clearly over ASC-10U10Mn, while those same bands were barely visible in the spectra of ASC-

10Mn. The band at 1085 cm^{-1} assigned to coordinated NH_3 on Lewis acid sites was present in the spectra of both catalysts, but the intensity for ASC-10U10Mn was much higher than ASC-10Mn. After passing the gas mixture of NO and O_2 , this band disappeared immediately over ASC-10U10Mn, but remained over ASC-10Mn with weak intensity, suggesting less coordinated NH_3 available to participate in the LT SCR reaction. Nitrogen doping not only provided more active sites to adsorb ammonia species, but also promoted coordinated NH_3 for the SCR reaction.

The spectra of ASC-10U10Mn were compared at different temperatures, as shown in Fig. 9(c). When the catalyst was exposed to NH_3 at lower temperatures, the intensity of the bands at 1085 , 1540 , 1552 , and 1649 cm^{-1} vanished to varying degrees. In particular, the band at 1540 cm^{-1} assigned to amide species changed significantly. Amide species are possibly more active than other adsorbed ammonia species at low temperatures. The bands at 1374 and 1634 cm^{-1} assigned to free nitrate ions and either gas phase or weakly adsorbed NO_2 were also affected by temperature as the gas mixture of NO and O_2 was purged in the reaction chamber.

SCR steady-state reaction. The formation of surface species on the ASC-10U10Mn in an SCR atmosphere was also examined. Besides the bands at 965 and 930 cm^{-1} , coordinated NH_3 and NH_4^+ species were again detected at 1085 , 1624 , and 1685 cm^{-1} . The band at 1174 cm^{-1} assigned to $\text{cis-N}_2\text{O}_2^{2-}$ was observed in steady state conditions. In addition, the presence of bidentate nitrate and bridging nitrite was suggested due to the observation of bands at 1220 and 1235 cm^{-1} , respectively (Yu et al., 2017). Bridging nitrates at 1610 cm^{-1} were consumed as monodentate nitrates appeared at 1591 cm^{-1} . Certainly, H_2O with a strong band in the range $3420\text{--}3750\text{ cm}^{-1}$ also appeared, and the intensity of this band continued to increase, indicating

that the SCR reaction had taken place. Bridging nitrate at 1235 and 1610 cm^{-1} was consumed in the first 5 min after ammonia was introduced, and then gradually accumulated until reaching a steady state. Considering the changes of bands at 1540 and 1552 cm^{-1} in above single experiments, $-\text{NH}_2$ participated in the LT SCR reaction continuously and played an important role based on the significant decrease in intensity of bands assigned to intermediates $-\text{NH}_2$ at the SCR steady-state experiment. In addition, the bands assigned to $\text{C}=\text{O}$ vibrations and $\text{C}=\text{C}$ bonds in an aromatic ring could also be observed at 1778(1430) and 1715 cm^{-1} , but the changes of the atmosphere barely have effects on these bands.

3.3 Mechanism discussion

It is common knowledge that the morphology and structural features of catalysts are directly related to catalytic performance. Based on the preceding analysis, nitrogen doping indeed optimized the morphology of ASC-10U10Mn. However, ASC-10U10Mn with surface area of 38.0 m^2/g and total pore volume of 0.026 cm^3/g has the superior catalytic performance compared with other samples. It is not consistent with the typical expectation that developed pores promote the activity of a catalyst by providing larger surface area and pore volume (Lu et al., 2018). This implies that in addition to the morphology and structure, internal chemical properties also play a vital role in promoting catalytic performance in the LT SCR reaction. Based on the above DRIFTS results, it can be confirmed that NH_3 species were adsorbed over ASC-10U10Mn by different paths, as described by Equations (1)–(4). Gaseous NH_3 is initially adsorbed on Lewis acid sites to form coordinated NH_3 , and also on Brønsted acid sites, leading to the appearance of NH_4^+ . The literature (Yu et al., 2017; Chen et al., 2015) suggests that

adsorbed NH_3 on Lewis acid sites plays an important role in the SCR reaction. For ASC-10U10Mn, this is reflected in the obvious changes of the stable bands at 1085 and 1624 cm^{-1} assigned to coordinated NH_3 in Fig. 9(a), indicating that coordinated NH_3 on Lewis acid sites is more active than NH_4^+ on Brønsted acid sites. Besides, nitrogen doping provided the abundant nitrogen functional groups and improved O_β concentration on ASC-10U10Mn. The mobility of electrons between manganese in different valences could improve via the presented oxygen bridge of Mn-O-Mn on ASC-10U10Mn, which would promote the generation of oxygen vacancy. It could be one reason that nitrogen doping promoted the SCR performance of ASC-10U10Mn. Hence, coordinated NH_3 could be oxidized to form the new amide species ($-\text{NH}_2$) intermediates.

A previous study (Ramis et al., 1990) has proposed that the formation of $-\text{NH}_2$ is a vital step in the LT SCR reaction. As shown in the IR spectra, the intensity of the bands assigned to $-\text{NH}_2$ rapidly decreased upon introduction of NO and O_2 into the reaction chamber. The $-\text{NH}_2$ species exhibited weak peaks in the SCR steady-state reaction, and we suggest that $-\text{NH}_2$ species are actively contributing to the LT SCR reaction. Gas phase or weakly adsorbed NH_3 is continually transferred to coordinated NH_3 and NH_4^+ , which is consistent with the dramatic decrease in intensity of the bands at 965 and 930 cm^{-1} . In this study, the intensity of the bands assigned to NH_4^+ decreased slightly, implying that NH_4^+ reactivity was relatively low. By comprehensively

considering the changes of adsorbed NH_3 species, it can be concluded that coordinated NH_3 and $-\text{NH}_2$ species play an important role in the SCR reaction.

In general, NO can be adsorbed over ASC-10U10Mn due to the intrinsic π -bonds and functional groups. XPS characterization reveals a greater abundance of pyridinic-N, pyrrolic-N, and quaternary-N as active sites over ASC-10U10Mn. The unpaired electrons in N-6 and N-5 acting as “Lewis bases” are available for interaction with empty π -antibonding orbitals in the NO molecule (Wang et al., 2018; Qiu et al., 2018), which can promote NO adsorption. The adsorbed NO can then be further oxidized to NO_2 , $\text{cis-N}_2\text{O}_2^{2-}$, and $-\text{NO}_3^-$ to maintain the turnover of redox reactions in the SCR process. The oxidation of NO develops via the L-H mechanism and is the limiting step for the SCR reaction. Combined with the XPS results, it can be surmised that the increased NO conversion of ASC-10U10Mn is closely related to the enhanced oxidation of NO.

The intermediates derived from the NO adsorption of these nitrogen functional groups can be

further reduced by coordinated NH_3 or $-\text{NH}_2$ species; accordingly, the intensity of the bands assigned to the pyridinic and pyrrolic decreased gradually, as reflected in the IR spectra. In addition to the fact that gaseous or weakly adsorbed NO and NO_2 can be detected successively, some nitrate species were generated and kept stable (1610, 1591, 1322, 1235, and 1220 cm^{-1} in Fig. 9(a)). The generated nitrate species on the catalyst could be described as follow:

As shown in Fig. 9(a), bridging nitrate apparently existed over ASC-10U10Mn in 5min as passing NO and O_2 ; bidentate nitrate then formed and was stable for 30 min. Yu et al. (Yu et al., 2017) reported that bidentate nitrate can occupy active sites but cannot react with NH_3 , which agrees with the increasing accumulation of the bands assigned to bidentate nitrate and the subsequent formation of monodentate nitrate when the SCR gas passed through the catalyst. Although bidentate nitrate is inactive in the LT SCR reaction, it can be affected by NH_3 . Qi et al. and Peña et al. (Qi et al., 2004; Peña et al. 2004) explained that a similar phenomenon is possibly caused by electron transfer between NH_3 and nitro species. Therefore, it is reasonable to deduce that the role of pyrrolic-N and quaternary-N over ASC-10U10Mn should not be

neglected in the LT SCR reaction. Additionally, as an essential intermediate, bridging nitrate promotes the evolution of the LT SCR process; the reaction scheme can be described as Equation (12) and (13), which is consistent with previous studies (Chen et al., 2015). Based on the comparison in Fig. 9(b), there are more adsorbed NH_3 species and nitrate species on ASC-10U10Mn than on ASC-10Mn. NH_3 -TPD analysis also proved the existence of abundant Lewis acid sites on the catalyst from nitrogen doping, which plays an important role in the enhancement of NH_3 adsorption and is related to the LT SCR activity. This demonstrates that ASC-10U10Mn contains more active sites than ASC-10Mn, since nitrogen doping supplies an abundance of nitrogen functional groups and promotes electron transfer. Accordingly, LT SCR performance is significantly promoted by nitrogen doping. The promotional mechanism of nitrogen doping on MnO_x /semi-coke catalyst can be summarized as Fig. 10.

Fig.10 Promotional mechanism of nitrogen doping on MnO_x/semi-coke catalyst for LT SCR

4. Conclusion

In summary, nitrogen doping on MnO_x/semi-coke catalysts results in markedly improved NH₃-SCR catalytic performance at low temperatures. The NO conversion of the ASC-10U10Mn catalyst was > 50% at 125°C and higher, and exhibited the optimum of 94.5% at 275°C. Besides the morphology and structure, nitrogen doping can promote the SCR reactivity of the catalyst by influencing the internal chemical properties. The formation of nitrogen functional groups led to the enhanced electron mobility and further promoted the oxidation of coordinated NH₃. The generation of intermediate -NH₂ species is critical in the LT SCR reaction. And the presence of pyridinic-N and pyrrolic-N is especially beneficial to adsorb NO and contributes to the transformation of inactive bidentate nitrate species. The formation of bridging nitrates could also accelerate the reaction with adsorbed NH₃ species and be favorable for further LT NH₃-SCR reaction.

CRedit author statement

Lu Yao: Conceptualization, Methodology, Writing-Original draft preparation, Investigation, Formal analysis

Qingcai Liu: Supervision, Methodology, Resources, Funding acquisition

Susanne Mossin: Methodology, Resources, Writing-Review & Editing

David Nielsen: Investigation, Visualization

Ming Kong: Validation, Writing-Review & Editing

Lijun Jiang: Investigation, Formal analysis, Validation,

Jie Yang: Investigation, Formal analysis, Writing-Review & Editing

Shan Ren: Conceptualization, Funding acquisition, Project administration

Juan Wen: Resources, Investigation, Writing-Review & Editing

Declaration of interests

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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