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Nitrogen doping of activated carbon loading Fe_2O_3 and activity in carbon-nitric oxide reaction

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Abstract: Nitrogen doping of activated carbon loading Fe_2O_3 was performed by annealing in ammonia, and the activity of the modified carbon for NO reduction was studied in the presence of oxygen. Results show that Fe_2O_3 enhances the amount of surface oxygen complexes and facilitates nitrogen incorporation in the carbon, especially in the form of pyridinic nitrogen. The modified carbon shows excellent activity for NO reduction in the low temperature regime (<500 °C) because of the cooperative effect of Fe_2O_3 and the surface nitrogen species.

Key words: Activated carbon, Nitric oxide, Doping, Iron oxides, Catalytic reduction

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INTRODUCTION

The reduction of NO_x with carbonaceous materials is an interesting field, and the reaction of C-NO was investigated extensively (Aarna and Suuberg, 1997; Gupta and Fan, 2003; Liu *et al.*, 2006; Bueno-López *et al.*, 2006; Klose and Rincón, 2007). Physical and chemical characters of carbons have great effects on the reduction of NO by carbons since it is a heterogeneous reaction. In recent years, study on the role of surface nitrogen species in C-NO reaction is an attractive object. Suzuki *et al.*(1994) found that a considerable amount of nitrogen was trapped in the carbon matrix during C-NO reaction, with the surface nitrogen species being able to react with NO (Chambrion *et al.*, 1997). The study by Matzner and Boehm (1998) showed that nitrogen doping of carbons could enhance the reactivity in the reduction of nitrogen oxides. All of these show that surface nitrogen species play an important role in C-NO reaction.

The potentially applicable perspective of nitrogen-enriched carbons has resulted in some attempts at its preparation (Pietrzak *et al.*, 2006). Some studies indicated that surface oxygen species could facilitate nitrogen incorporation in carbons (Suzuki *et al.*, 1994; Szymański *et al.*, 2004; Pietrzak *et al.*, 2006). Generally, some precursors of activated carbons, such as coals and chars, contain mineral matters in nature, but the effect of these impurities on nitrogen doping of the carbons is unclear as well as the dual effect of surface nitrogen groups and the mineral matters on NO reduction by the carbons. In this work, nitrogen doping of the carbon loading Fe_2O_3 is performed by annealing in ammonia, and the effect of Fe_2O_3 on the content and state of surface nitrogen species is investigated as well as the cooperative effect of Fe_2O_3 and the surface nitrogen species on NO reduction by the modified carbons.

EXPERIMENTAL SECTION

Synthesis of carbon and characterization

The demineralized activated carbons (AC) were provided by National Pharmaceutical Group Corpo-

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ration, in particle size of 0.9~1.2 mm. The carbon loading Fe_2O_3 (ACFe) was prepared by immersing AC in an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ at ambient temperature for 24 h and drying it at 110 °C followed by calcining in argon at 500 °C for 2 h. Nitrogen was incorporated in the carbons by annealing in ammonia at 500 °C for 2 h and cooled in argon, by which ACN and ACFeN were obtained. All samples were stored in ambient air.

Specific surface area and porous structure were determined by N_2 adsorption at −196 °C using a Quantachrome Autosorb-1-C instrument. Elemental analysis of all carbons was performed using a ThermoFinnigan Flash EA1112 element analyzer. XRD characterization was conducted using a Rigaku D/MAX-RA diffractometer with Cu-Kα radiation. XPS analysis was performed using a PHI1600 XPS system operated at 1.2×10^{-8} Torr under Mg-Kα radiation.

Reduction of NO by carbons

The NO reduction by carbons was performed in a 1.5 cm diameter quartz fixed-bed reactor over a temperature range of 200~800 °C under the following conditions: gas velocity: 300 ml/min; mass of carbons: 300 mg; gas pressure: 1.01325×10^5 Pa; reactant gases composition: 0.1% NO, 0.6% O_2 with the rest being argon. The carbons were preheated in argon at 800 °C for 30 min and cooled to reaction temperature. Then reactant gases were introduced. The total concentration of NO_x (including NO and NO_2) in products was analyzed using a Kane International Limited Model KM9106 NO_x analyzer. The experimental error was within ±5%.

RESULTS AND DISCUSSION

Characterization of the carbons

Table 1 shows all carbons possess similar porous architecture. Compared with AC, a small decrease in surface area (S_{BET}) and the total pore volume (V_t) of ACFe that was observed, should be attributed to the blockage of pore entrances by Fe_2O_3 particles. After the thermal treatment in ammonia, the surface area of ACFeN increases by about 10% as well as the micropore volume (V_{mic}), but such a situation did not occur in ACN. As we all know, carbon can be activated by chemical method, so this should be a consequence of activation of the carbon by iron oxides during annealing in ammonia.

Table 1 Structural parameters of the carbons

Carbon	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mic} (cm^3/g)	V_{meso} (cm^3/g)	D_{ap} (nm)
AC	801	0.470	0.392	0.078	2.35
ACN	805	0.443	0.394	0.039	2.20
ACFe	721	0.381	0.355	0.026	2.11
ACFeN	792	0.421	0.393	0.028	2.13

D_{ap}: Average pore diameter

The elemental analysis of all carbons is presented in Table 2. Both AC and ACN are ashless, and the ash composition of ACFe and ACFeN is iron oxides. The elemental contents of C^a, H^a, N^a are obtained on a dry-ash-free basis, and the content of $O^{a,b}$ is calculated by difference. The data show that the contents of C^a and N^a increase at the expense of H^a and $O^{a,b}$ after thermal treatment in ammonia. The content of nitrogen in the bulk of the carbons is in the order of ACFeN>ACN>ACFe=AC, and that of ACFeN is as high as 1.4 wt.%. This shows that nitrogen is incorporated in the carbons during thermal treatment in ammonia.

Table 2 Elemental analysis of the carbons

Carbon	Content (wt.%)				
	ash^a	C^a	H^a	N^a	$O^{a,b}$
AC	0	89.2	1.0	0.3	9.5
ACN	0	91.5	0.5	0.8	7.2
ACFe	2.0	89.7	0.9	0.3	9.1
ACFeN	2.0	91.6	0.7	1.4	6.3

[a] Dry-ash-free (daf) basis; [b] Determined by difference

XPS measurements were performed to characterize the changes taking place on the surface of the carbons and the results are listed in Table 3. The surface nitrogen contents of the carbons increase greatly after thermal treatment in ammonia, which is the same as the result of the elemental analysis. As we all know, surface oxygen species can facilitate nitrogen incorporation in carbons (Suzuki *et al.*, 1994; Szymański *et al.*, 2004; Pietrzak *et al.*, 2006), and it was also observed in this experiment. The data in Table 3 show that the surface nitrogen content of ACFeN is higher than that of ACN while its precursor possesses higher surface oxygen content. This indicates that iron oxides should be responsible for the higher nitrogen content of ACFeN since iron oxides enhance the amount of surface oxygen complexes.

Table 3 Chemical surface composition obtained by XPS, disregarding hydrogen

Carbon	Surface composition (at.%)			
	C	N	O	Fe
AC	91.4	0.7	7.9	—
ACN	93.8	2.5	3.7	—
ACFe	78.9	0.8	16.2	4.1
ACFeN	78.3	4.2	13.7	3.8

In order to investigate the effect of Fe_2O_3 on the state of the surface nitrogen groups in the ammonia treatment, high-resolution N 1s spectra were obtained over the 396~405 eV range (Biniak *et al*., 1997; Huang and Teng, 2003; Szymański *et al*., 2004). The spectra in Fig.1 reveal the presence of four distinct nitrogen functionalities corresponding to pyridinic nitrogen (N-6, *BE*=398.4~398.7 eV), pyrrolic or pyridonic nitrogen (N-5, *BE*=400.1~400.4 eV), quaternary nitrogen in aromatic graphene structure (N-Q, *BE*=401.9 eV), and pyridine-N-oxides structures (N-X, *BE*=402 eV). The contribution of nitrogen species to the N 1s peaks is shown in Table 4 indicating that major nitrogen species are N-5 and N-Q in AC, and those of ACFe are N-5 and N-Q as well as N-6. After thermal treatment in ammonia, their N-Q peaks disappear just as shown in Fig.1, and the major nitrogen species are N-5 and N-6 in both ACN and ACFeN. This shows that N-Q translates to the other nitrogen species, due to the removal of the surrounding carbon during annealing in ammonia (Kapteijn *et al*., 1999), and that almost all nitrogen atoms incorporated in the carbon matrix locate at the edges of graphene structures in the form of N-5 and N-6. Furthermore, pyridine-N-oxides structures are also present in ACFeN, which may be ascribed to oxidization of N-6 by the surface oxygen species, but the phenomenon did not appear in ACN and the other carbons, which may be related to the higher contents of both nitrogen and oxygen in ACFeN just as shown in Table 3.

Table 4 Contribution of nitrogen species to the N 1s peak

Carbon	Contribution of nitrogen species (%)			
	N-6	N-5	N-Q	N-X
AC	16.3	53.3	30.4	—
ACN	39.5	60.5	—	—
ACFe	23.3	45.0	31.7	—
ACFeN	43.2	43.1	—	13.7

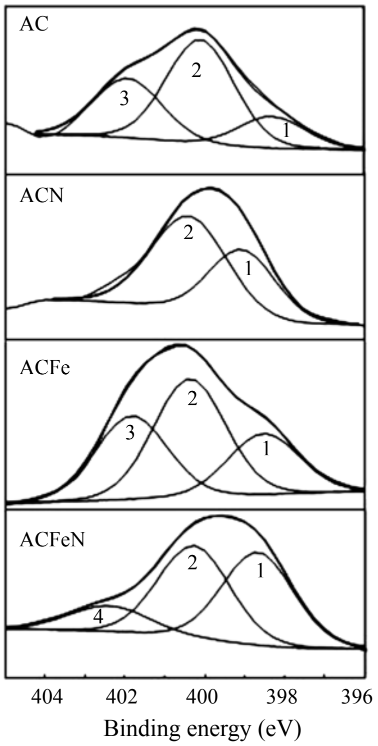

Fig.1 XPS N 1s spectra of the carbons
(1) N-6, (2) N-5, (3) N-Q, (4) N-X

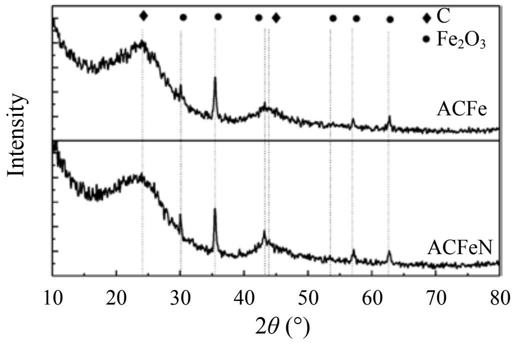

Fig.2 XRD patterns of ACFe and ACFeN

Fig.2 gives the XRD patterns for ACFe and ACFeN. The wide dispersion peaks in the range of 20°~30° and 40°~50° are characteristic peaks for carbon. Both carbons have sharp peaks at 30.2°, 35.5°, 43.3°, 57.2° and 62.8° which are attributed to the cubic Fe_2O_3 crystal. The particle size of Fe_2O_3 calculated using Scherrer formula is 23 nm for ACFe, and 24 nm for ACFeN. The chemical state and particle size of the iron oxides do not change before and after the ammonia treatment.

Reduction of NO by different carbons

Fig.3 presents a comparison of reaction activity of all carbons for NO reduction in the presence of oxygen. Obviously, the activity of the carbons increases remarkably after the ammonia treatment, even the activity of ACN is much higher than that of ACFe in the low temperature regime (<500 °C). This shows that nitrogen content has a positive effect on the activity of the carbons, and it is believed that surface nitrogen species act as catalytic active centers and help the forming of reactive intermediates (Matzner and Boehm, 1998; Huang and Teng, 2003).

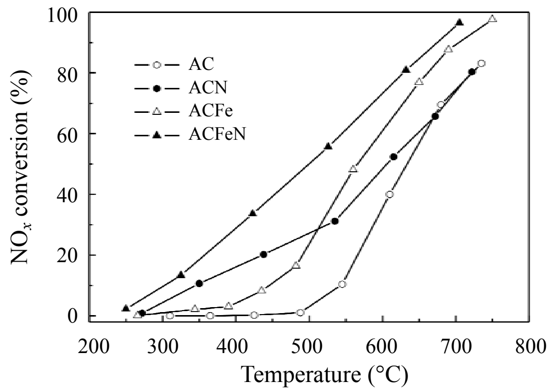

Fig.3 Activity of different carbons in NO reduction

It is observed that there is a break in NO_x conversion for ACN at near 535 °C, and that this temperature is close to starting temperature of NO reduction by AC. When temperature is above 535 °C, active carbon sites (C_f) obtained continuously can facilitate NO reduction as surface nitrogen species (C(N)) do it, so the high activity of ACN should be ascribed to the dual effect of C(N) and C_f on the reduction of NO. When the temperature is above 650 °C, the activity of AC is close to that of ACN, which can be explained by the decomposition of C(N) in the high temperature (Suzuki *et al.*, 1994). Regarding the curve of ACFeN, a break appears at 320 °C instead of 535 °C. The impregnation of Fe_2O_3 should be responsible for the shift of the break to low temperature, since the catalytic reduction of NO by carbon loading Fe_2O_3 can be performed at low temperature just as Fig.3 shows (Illán-Gómez *et al.*, 1999). Furthermore, it would be worthwhile to mention the cooperatively catalytic effect of C(N) and Fe_2O_3 in NO reduction by ACFeN. Fe_2O_3 shows desirable catalytic activity over the experimental temperature range, and C(N) does it in the low temperature regime, but higher NO_x conversion can be achieved over ACFeN in the low temperature regime because of the cooperative effect of C(N) and Fe_2O_3.

CONCLUSION

The present work shows that Fe_2O_3 loaded in the carbon enhances the amount of surface oxygen complexes, and facilitates the nitrogen incorporation in the carbon during the ammonia treatment. Almost all nitrogen atoms incorporated in the carbon locate at the edges of the graphene structures, especially in the form of pyridinic nitrogen structures. The reduction of NO by the modified carbon begins at a low temperature, and the modified carbon shows excellent activity in the low temperature regime (<500 °C) because of the cooperative effect of C(N) and Fe_2O_3 in C-NO reaction. This work will give an idea for preparation of nitrogen-enriched carbons possessing excellent activity for NO reduction in low temperature regime, which is important for its practical application.

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