Journal of Zhejiang University SCIENCE A
ISSN 1673-565X (Print); ISSN 1862-1775 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Science Letters:

Effect of nitrogen doping on the reduction of nitric oxide with activated carbon in the presence of oxygen

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Received July 20, 2007; revision accepted Oct. 20, 2007; published online Nov. 25, 2007

Abstract: Nitrogen doping of activated carbon (AC) was performed by annealing both in ammonia and nitric oxide, and the activities of the modified carbons for NO reduction were studied in the presence of oxygen. Results show that nitrogen atoms were incorporated into the carbons, mostly in the form of pyridinic nitrogen or pyridonic nitrogen. The effect of nitrogen doping on the activities of the carbons can be ignored when oxygen is absent, but the doped carbons show desirable activities in the low temperature regime (≤500 °C) when oxygen is present. The role of the surface nitrogen species is suggested to promote the formation of NO_2 in the presence of oxygen, and NO_2 can facilitate decomposition of the surface oxygen species in the low temperature regime.

Key words: Activated carbon (AC), Nitric oxide, Doping, Reduction
doi:10.1631/jzus.A073019 **Document code:** A **CLC number:** X5; TQ53

INTRODUCTION

The reduction of NO with carbonaceous materials is such an interesting subject that it is investigated extensively both in the deNO$_x$ of fuel gas and the desoot-deNO$_x$ of automotive exhaust gas (Aarna and Suuberg, 1997; Gupta and Fan, 2003; Setiabudi *et al.*, 2004; Jeguirim *et al.*, 2005; Liu *et al.*, 2006; Klose and Rincón, 2007; Muckenhuber and Grothe, 2007). Since the NO-C reaction is a heterogeneous reaction, the surface chemistries of the carbons have great effects on the reactivity of the carbons. Many studies have focused on the effect of both surface oxygen species and metallic catalysts on the reduction of NO with carbons. In recent years, it was found that surface nitrogen species could also play an important role in the formation of N_2 (Suzuki *et al.*, 1994; Chambrion *et al.*, 1997; Matzner and Boehm, 1998; Tomita, 2001; Wan *et al.*, 2007). The effect of surface nitrogen species on the reaction is often investigated in the absence of oxygen, but the situation in the presence of oxygen is still unclear. In this work, nitrogen atoms are incorporated into carbons by thermal treatment both in ammonia and nitric oxide, and the effect of nitrogen doping on the reduction of nitric oxide with activated carbon is studied in the presence of oxygen, and a possible mechanism is discussed.

EXPERIMENTAL SECTION

Synthesis of the carbons and characterization

An ashless activated carbon (AC) was used as the starting material in particle sizes of 0.9~1.2 mm. The nitrogen doping of the carbon was performed by two methods. The carbon N-AC-1 was prepared by thermal treatment of AC in ammonia at 500 °C for 4 h, and carbon N-AC-2 was prepared by thermal treatment of AC in 0.1% NO+balance Ar at 600 °C for 4 h. Specific surface area and porous structure were determined by N_2 adsorption at −196 °C using a Quantachrome Autosorb-1-C instrument. Elemental

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analysis of all carbons was performed using a ThermoFinnigan Flash EA1112 element analyzer. XPS analysis was performed using a PHI1600 XPS system operated at 1.2×10^{-8} Torr under Mg-K_α 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 200~900 °C. The composition of reactant gases for NO reduction in the presence of oxygen was 0.1% NO+0.6% O_2+balance Ar, and that in the absence of oxygen was 0.1% NO+balance Ar. The 300 mg carbon was preheated in argon at 900 °C for 30 min and cooled to reaction temperature, and then 300 ml/min reactant gases were introduced. The gas pressure was 1.01325×10^5 Pa. 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 carbons

Table 1 shows that all carbons possess similar structures. Compared with AC, the specific surface areas (S_{BET}) of two modified carbons, as well as the total pore volume (V_{t}) and the micropore volume (V_{mic}), have a small increase, which should be ascribed to the effect of the thermal treatment, but the change of both the mesopore volume (V_{mes}) and the average pore diameter (D_{ap}) could be ignored.

Table 1 Textural characterization of the carbons

Carbon	S_{BET} (m^2/g)	V_{t} (cm^3/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	D_{ap} (nm)
AC	824	0.495	0.412	0.083	2.23
N-AC-1	892	0.523	0.444	0.079	2.16
N-AC-2	839	0.502	0.420	0.082	2.21

The elemental analysis of the carbons is presented in Table 2. The elemental contents of carbon, hydrogen, and nitrogen were obtained on a dry-ash-free (daf) basis, and the oxygen content was calculated by difference. As expected, the nitrogen content increased at the expense of oxygen after nitrogen doping of the carbons. The nitrogen content in the carbons decreased in the order of N-AC-1> N-AC-2>AC, and that of N-AC-1 took a value of 2.1 wt%. In order to further analyze the surface chemistry, especially the nitrogen species, XPS was employed. A quantitative analysis of surface nitrogen content was carried out and the results are listed in Table 3. It is obvious that the surface nitrogen contents are higher than those in the bulk. The results show that most of nitrogen atoms incorporated into the carbons were located at the external portion.

Table 2 Elemental analysis of the carbons

Carbon	Content (wt%)			
	C[a]	N[a]	O[a,b]	H[a]
AC	90.0	0.4	8.9	0.7
N-AC-1	92.9	2.1	4.5	0.5
N-AC-2	91.5	0.8	7.3	0.4

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

Table 3 Surface and bulk nitrogen content of the carbons and the contribution of surface nitrogen species to N 1s peak

Carbon	Nitrogen content (at.%)		Contribution to N 1s peak (%)			
	Bulk	Surface	N-6	N-5	N-Q	N-X
AC	0.4	0.6	28.8	52.6	18.6	—
N-AC-1	1.8	4.4	38.3	34.0	18.8	8.9
N-AC-2	0.7	1.8	41.6	37.3	21.1	—

The high-resolution N 1s spectra were obtained over the 394~406 eV range (Biniak *et al*., 1997; Szymański *et al*., 2004). The spectra in Fig.1 reveal the presence of four distinct nitrogen functionalities corresponding to pyridinic nitrogen (N-6, binding energy (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=404 eV). The contribution of nitrogen species to the N 1s peaks is shown in Table 3. The major surface nitrogen species of both modified carbons were N-6 and N-5. Most of the nitrogen atoms incorporated into the carbons were located at the edges of graphene structures in the form of stable complexes.

Reduction of NO by carbons

The activity of carbons in the presence of oxygen is presented in Fig.2a. The reduction of NO became noticeable at about 300 °C with the doped carbons.

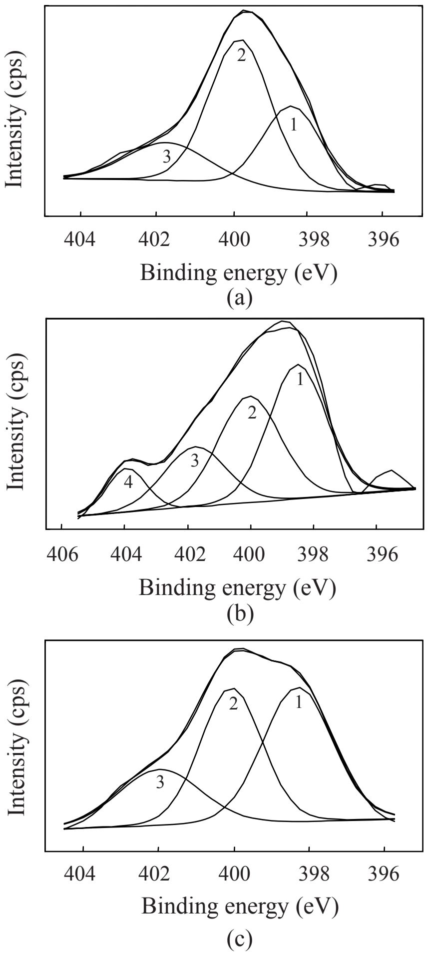

Fig.1 XPS N 1s spectra of the carbons. Curve 1: N-6; Curve 2: N-5; Curve 3: N-Q; Curve 4: N-X. (a) AC; (b) N-AC-1; (C) N-AC-2

With AC, the reaction began at about 500 °C. The NO_x conversion with N-AC-1 was about 16% at 500 °C, and that with N-AC-2 was about 12%. It is clear that the nitrogen doping of carbon facilitates the reduction of NO with carbons in a low temperature regime (≤500 °C). When the temperature was above 600 °C, nitrogen doping of the carbons had an inhibiting effect on the reduction of NO. It suggests that the surface nitrogen species were converted to NO_x. This result supports the theory that surface nitrogen species can easily be removed in NO- or O_2-containing reaction atmosphere at high temperature (Suzuki *et al.*, 1994).

In order to investigate the effect of oxygen on reduction of NO with doped carbons, the activity of carbons in the absence of oxygen was also studied and the results are presented in Fig.2b. With N-AC-1, the NO_x conversion was about 4% at 500 °C, while the positive effect was not observed in the case of N-AC-2. It is obvious that the activity of the doped carbons in the presence of oxygen is higher than that in the absence of oxygen, but it should not attribute to single effect of oxygen, because the effect of oxygen on the activity of AC can be ignored in the low temperature regime.

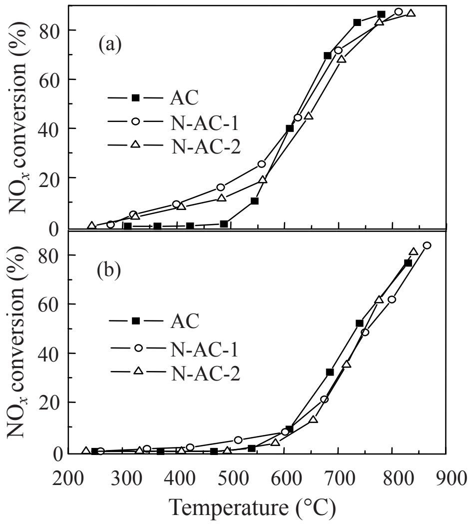

Fig.2 Effect of nitrogen-doping on the activities of activated carbons. (a) 0.1% NO+balance Ar; (b) 0.1% NO+0.6% O_2+balance Ar

In the presence of oxygen, it seems reasonable to suppose that reactive intermediates are formed onto the surface of doped carbons in the low temperature regime. According to some studies (Stöhr *et al.,* 1991; Huang and Teng, 2003; Szymański *et al.*, 2004), surface nitrogen species (RC(N), R denotes carbon surface), as catalytic active centers, may facilitate the formation of NO_2 due to molecular oxygen activation according to reactions (1) and (2):

$$RC(N)+O_2 \rightleftharpoons RC(N^+\text{---}O_2^-), \quad (1)$$

$$RC(N^+\text{---}O_2^-)+2NO \rightarrow RC(N)+2NO_2. \quad (2)$$

According to the mechanism of the reduction of nitric oxide with carbon, carbon free active-site (RC_f and $R'C_f$) plays an important role in the reduction of NO with carbons. The chemisorptions of both O_2 and NO onto the surface of carbon can take place according to reactions (3) and (4), and the carbon free active-sites can be regenerated by the decomposition of surface oxygen species ($RC_f(O)$) according to reactions (5) and (6) at high temperature. The decomposition of $RC_f(O)$ is often seen as the rate-determining step for the chemisorption of NO in the low temperature regime.

$$2RC_f + O_2 \rightarrow 2RC_f(O), \quad (3)$$

$$2RC_f + 2NO \rightarrow 2RC_f(O) + N_2, \quad (4)$$

$$2RC_f(O) + O_2 \rightarrow 2R'C_f + 2CO_2, \quad (5)$$

$$2RC_f(O) \rightarrow 2R'C_f + CO_2, \quad (6)$$

$$RC_f(O) + NO_2 \rightarrow R'C_f + NO + CO_2. \quad (7)$$

NO_2 is a stronger oxidant than O_2, and it can facilitate the decomposition of neighboring $RC_f(O)$ according to reaction (7), and the desired carbon free active-site for reaction (4) can be obtained at lower temperatures (Zawadzki *et al.*, 2003; Setiabudi *et al.*, 2004; Muckenhuber and Grothe, 2006; Azambre *et al.*, 2006), so the reduction of NO with the carbons may become easier when NO_2 is present. The formation of NO_2 is probably the rate-determining step for the reduction of NO with the doped carbons in the low temperature regime.

The effect of NO_2 on the reduction of NO with AC is presented in Fig.3. When reaction gases change from $NO/O_2/Ar$ to $NO/NO_2/O_2/Ar$, the starting temperature decreased from 500 °C to 300 °C, and the activity of AC has a great increase in the low temperature regime. It is interesting to find that the activity curve of AC in the presence of NO_2 is similar to that of the doped carbons in the presence of O_2, and that the result supports the hypothesis.

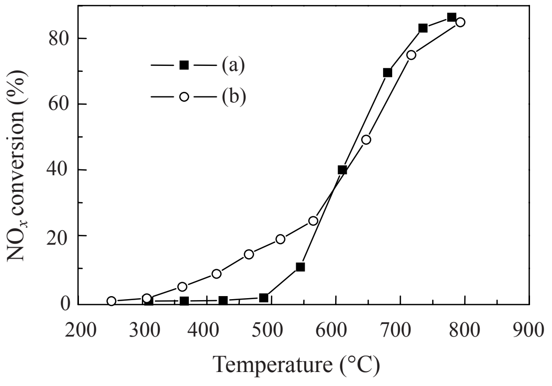

Fig.3 Effect of NO_2 on the reduction of NO with AC
(a) 0.1% NO+0.6% O_2+balance Ar; (b) 0.08% NO+0.02% NO_2+0.6% O_2+balance Ar

CONCLUSION

The present work shows that the surface nitrogen contents of the carbons are increased by nitrogen doping, especially in the form of N-6 and N-5. Nitrogen doping of the carbons facilitates the reduction of NO with the carbons in the presence of oxygen in a low temperature regime (≤500 °C), but the same results were not observed in the absence of oxygen. The possible role of surface nitrogen species is to facilitate the formation of the active intermediate NO_2 in the presence of oxygen.

PROSPECT

Our teams think this paper is an important work which will help to explain the real role of surface nitrogen species in the reduction of NO with carbon when oxygen is present. More details of the reaction at the molecular level, especially the formation of the N-N bond onto the surface of the doped activated carbon, will be further studied.

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