NH₃-activated carbon nanofibers for low-concentration NO removal at room temperature

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Abstract:

Nitrogen-doped carbon nanofibers (NCNFs) were prepared by activating [electrospun carbon nanofibers](#) using NH₃ as activating agent at different temperatures. NCNFs with various contents of nitrogen were used as adsorbents and catalysts for low-concentration NO removal at room temperature. The NO removal efficiency over NCNFs was far above that over porous carbon nanofibers obtained by steam-activation, suggesting that NCNFs are efficient catalysts for low-concentration NO removal at room temperature. A maximum of 64.5% removal efficiency for NO was acquired at NO initial concentration of 20 ppm and 21 vol% of O₂ at room temperature.

Key words: Nitrogen-doped carbon nanofibers (NCNFs); NO removal; catalytic oxidation

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1. Introduction

Nitrogen oxides (NO_x , mainly as NO and NO_2) emitted from anthropogenic activities are considered as primary atmospheric pollutants, because NO_x can deteriorate the environmental and human health^[1, 2]. Numerous environmental issues, e.g. acid rain, ozone depletion and photochemical smog are ascribed to NO_x emissions^[3, 4]. With the society's increasing environmental awareness and implementation of more stringent NO_x emission regulations, it is imperative to control NO_x emissions and reduce the NO_x content in the atmosphere^[5, 6].

Up to now, considerable efforts have been devoted to removing NO , selective catalytic reduction (SCR)^[7] and NO_x storage/reduction (NSR)^[8] turning NO_x into N_2 are the most developed techniques NO_x control technology. Nevertheless, the working temperatures are far above room temperature (generally above 200°C) and they are effective only in removing high-concentration of NO_x , which hinder their application in the removal of low-concentration NO at room temperature. Thus, it is urgent to develop novel room-temperature NO -removal technologies. A promising alternative is to adsorb NO_x at room temperature. Unfortunately, it is challenge to adsorb NO owing to its super-low normal boiling point and inert chemical activities^[9-11]. Hence, a highly efficient catalyst that can catalytically oxidize NO into NO_2 at room temperature is in great need. Carbon materials are the promise catalysts for the oxidation of NO into NO_2 ^[12, 13], because activated carbon materials contain large number of micropores and high surface area and NO dimerization can be enhanced by micropores^[14], activated carbon materials are superior adsorbent for NO at low temperature^[15] and widely used as catalysts in the oxidation of NO ^[1, 5, 16, 17].

Unfortunately, the catalytic efficiency of traditional activated carbon materials (activated carbon, activated carbon fibers, etc.) will sharply decline at the decreased initial NO concentration down to less than 100 ppm, which indicates that they are suitable only for the oxidation of high-concentration NO in the case of fuel exhaust gases, not for the low-concentration NO of tens or less ppm in the case of road tunnels or indoor parks. In fact, it is extremely difficult to oxidize low-concentration NO into NO₂ at room temperature, because low-concentration NO of below 0.1 % is very inactive owing to the kinetic restriction ^[18]. In our previous studies, porous carbon nanofibers (PCNFs) prepared by steam activation were employed to remove low-concentration NO at room temperature^[19]. We found that low-concentration NO can be catalytically oxidized into NO₂ over PCNFs at room temperature, because PCNFs have high surface area and abundant micropores. To further improve the low-concentration NO oxidation conversion efficiency, PCNFs were graphitized and used as catalysts in oxidizing NO^[20] at room temperature, the oxidation conversion ratio of NO was enhanced significantly, while the adsorption capability decreased owing to the decrease of surface area and pore volume in the process of graphitization. Therefore, it is indispensable to develop novel PCNFs or modified PCNFs that have both excellent catalytic oxidation activity and adsorption capability toward NO.

Recent reports have shown that nitrogen-doped carbonaceous materials possess superior performance to pristine ones ^[21-23], because nitrogen is seen as N-type electron donator, the properties and performance of carbon materials can be tailored by adjusting nitrogen content. For example, nitrogen-doped carbon nanotubes (CNTs) exhibit higher activity for benzyl alcohol oxidation than the pristine CNTs ^[21], since the introduction of

electron-rich nitrogen atoms in the graphitic domains enhanced electron transfer which improved the catalytic activity. Nitrogen-doped graphene (N-graphene) also displayed better properties than pristine graphene, the synthesis, characterization and performance of N-graphene have been widely investigated^[22]. Furthermore, nitrogen-doped carbon nanofibers (NCNFs) exhibited high electrocatalytic activity, long-term operation stability and excellent tolerance in fuel cells^[23]. Recently, nitrogen-doped carbon xerogels were prepared from a nitrogen-containing polymer precursor via sol-gel process^[24], and they were excellent catalysts for NO oxidation at room temperature, for the presence of pyridine and pyrrole groups favored the oxidation of NO to NO₂.

Based on these, the objective of the present research was to (1) prepare nitrogen-doped carbon nanofibers (NCNFs) via NH₃ activation, (2) examine the low-concentration NO removal efficiency over NCNFs, and (3) explore the catalytic oxidation mechanism of low-concentration NO over NCNFs at room temperature.

2. Experimental section

2.1 NCNFs preparation

Polyacrylonitrile (PAN), the precursor of carbon nanofibers, was purchased from Scientific Polymer Products Inc. (USA), N, N-Dimethylformamide (DMF) was purchased from Sigma-Aldrich Co. Ltd. PAN nanofibers were prepared by electrospinning PAN/DMF solution with concentration of 10 wt%. The as-electrospun PAN nanofibers were firstly stabilized in air at 280 °C for 2 hours with a heating rate of 5 °C/min, then were carbonized at a set temperature for 20 minutes under N₂ atmosphere followed by activating via NH₃ with a flow rate of 200 SCCM for 30 minutes at 800, 850 and 900 °C, and the as-produced samples were designated as NCNF-800, NCNF-850 and

NCNF-900, respectively.

2.2. Characterization

Scanning electron microscopy (SEM) images of NCNFs were obtained on a LEO-1530 microscope to provide information regarding sample morphology. Textural structure of the samples was based on the N₂ adsorption isotherms determined at 77 K. The isotherms were collected on a Belsorp instruments (Belmax, Japan). Prior to the adsorption measurements, the samples were degassed at 473 K for 12 hours. The specific surface area of the samples was calculated by α_s -method^[25, 26], α_s -method is suitable for the evaluating the specific surface area of microporous materials. Micropore volume (V_{micro}), total pore volume (V_{total}) and pore size distribution are calculated using Quenched solid density functional theory (QSDFT)^[27-29]. Surface functional groups and elemental contents of these NCNFs were determined with X-ray photoelectron spectroscopy (XPS), the XPS spectra were obtained on a Thermo Scientific ESCALAB 250Xi system equipped with a dual X-ray source using Al-K α . All the binding energies were calibrated to a C1s peak located at 284.6 eV as a reference, peak fittings were achieved using Gaussian-Lorentzian equation assuming constant full width at half maximum for all the peaks.

2.3. NO removal test

The NO removal system is described in detail elsewhere^[19], it is briefly described here for clarity. The NO removal tests were performed in a fixed-bed quartz micro-reactor with an inner diameter of 6 mm using 0.1 g NCNFs sample for each test. The reaction temperature was maintained at 30 °C by a thermostatic water bath. The typical reactant gas composition was 20 ppm NO, 21 vol% O₂ and N₂ as balance gas.

Mass flow controllers (MFC) controlled the individual gas flow rates resulting in the specified [NO], [O₂], and total gas flow rate (200 SCCM) entering the reactor. The NO and NO₂ concentrations in the inlet and outlet gas were online measured and recorded by NO_x chemiluminescence analyzer of NO–NO₂–NO_x (Thermo Electron Co., USA, model 42i). Each test was operated at least 100 h to achieve steady-state outlet [NO] and [NO₂]. The NO removal ratio was calculated using equation (1), in which NO_{inlet} and NO_{outlet} represent the NO concentrations in the inlet and outlet gases, respectively.

$$NO\ removal\ ratio(\%) = \frac{NO_{inlet} - NO_{outlet}}{NO_{inlet}} \times 100\% \quad (1)$$

3. Results and discussion

Fig.1 displays the SEM images and fiber diameter distribution of porous carbon nanofibers activated with NH₃ at different temperatures. The diameters of the NCNFs were evaluated by selecting 50 fibers, the calculated average diameters for NCNF-800, NCNF-850 and NCNF-900 were 214, 194 and 86 nm. But the fiber diameter of PCNFs acquired from the same raw PAN nanofibers by steam activation at 800 °C is in the range of 200-500 nm^[19], which demonstrate that NH₃ activation tends to obtain thinner fibers. In comparison with CNFs carbonized at 800 °C without NH₃ activation (Fig.1d), it is easily observed that the surface of CNF is very smooth without pores, while the as-obtained NCNFs exhibited a rougher surface, smaller diameter and narrow fiber diameter distribution. Moreover, the diameter of NCNFs decreased with the increase of activation temperature, which is attributed to the strong etching reactivity of NH₃ with carbon^[23, 30]. NH₃ will decompose to generating H atoms or H-containing active species, and they are able to react with carbon and form carbon-containing active species or molecules, which result in the reduction of fiber diameter.

Fig.1 SEM images and fiber diameter distribution of porous carbon nanofiber activated with NH_3 at different temperatures: (a) NCNF-800 (b) NCNF-850 (c) NCNF-900 (d-1) CNF-850 (d-2) NCNF-850

N_2 adsorption-desorption isotherms and the quenched solid state functional theory (QSDFT)^[27] pore size distribution plots of these NCNFs activated at different

temperatures are shown in Fig.2. All the samples display typical I-type curves. With the increase of activation temperature, the N_2 adsorbed amount of these NCNFs increased gradually, the adsorbed amount increased slightly from 800 to 850 °C while increased dramatically from 850 to 900 °C. Based on N_2 adsorption/desorption isotherms, the calculated pore size distribution (PSD) curves by QSDFT methods suggest that all the NCNFs have defined microporosities. There is a sharp peak between 4 and 7 Å and a broad peak between 7 and 15 Å in the PSD plots of all three NCNFs. The total pore volume of these samples are 0.269, 0.295, 0.452 cm^3/g , and the micropore volume are 0.228, 0.236 and 0.407 cm^3/g , respectively, which indicated that NH_3 activation can obtain porous carbon nanofibers containing abundant micropores. The specific surface areas calculated by α_s method are 717, 725 and 1079 m^2/g .

Fig.2 (a) N_2 adsorption/desorption isotherms and (b) QSDFT pore size distribution plots of the NCNFs activated at different temperatures.

X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was employed to determine the composition and bonding states of the NCNFs. The XPS spectra of all the samples have three peaks shown in Fig.3a, such as predominant narrow graphitic C1s peak at 284.6 eV, along with an obvious N1s peak at 400.1 eV and O1s peak at 536.8 eV, which revealed that NH_3 activation can result in porous carbon nanofibers containing a

large amount of nitrogen. The surface element contents are summarized in Tab.1 according to XPS spectra. All the NCNFs consist of carbon, oxygen and nitrogen elements, and carbon is the main component and its content increased from 83.56 to 92.36 % when the activation temperature increased from 800 to 900 °C, while the nitrogen content reduced from 5.21 to 3.21 %.

Fig.3 (a) XPS survey spectra of NCNFs , (b) XPS of N1s of NCNFs, (c) XPS of C1s of NCNFs, (d) XPS of O1s of NCNFs

To investigate the effect of the temperature of NH_3 activation on the texture and surface groups of NCNFs, the N1s, C1s and O1s spectra of NCNFs are also presented here. Fig. 3b depicts the C1s peaks of three kinds of samples. The deconvolution of the peaks corresponding to carbon atoms in the C1s spectra shows three typical types of carbon bonds: C–C/C–H (285 ± 0.5 eV), C–O (286.5 ± 0.4 eV) and O–C=O (288.5 ± 0.4 eV)^[31]. Among the three peaks, the strongest peak located at 284.7 eV is contributed to

the combination of carbide, graphitic carbon and –OH. With the increase of carbonization temperature, the intensity and location of peaks changed accordingly. The most notable change is the peak at 289 eV, whose intensity reduced with the increase of activation temperature. All the N1s spectra of these samples consist of two obvious strong peaks, the first peak generally belongs to pyridinic-N group locating at 398 eV, the other broad peak locating around 401 eV actually contains two peaks involving pyrrolic-N at 400.9 eV and quaternary nitrogen at 401.1 ± 0.8 eV^[32]. It is obvious that the peak at 398 eV weakened while the peak at 401 eV enhanced, which indicated that temperature resulted in the change of nitrogen functional groups' relative contents. The ratio of pyrrolic-N and quaternary nitrogen to pyridinic-N increased from 1.66 to 1.74 and 2.06 when the activation temperature rose from 800 to 850 and 900 °C. For the O1s XPS spectra (Fig.3d), the peak located at 531.0 eV can be assigned to the oxygen atoms that bond with carbon form of C=O, the peak at 532.0 eV is attributed to C-O (C-OH and C-O-C) and the peak at 534.0 eV is ascribed to chemisorbed oxygen. When the activation temperature rose, the position of peaks shifted slightly.

Tab.1 Surface elements analysis of NCNFs

NCNFs	C (At.%)	O (At.%)	N (At.%)
NCNF-800	83.56	11.24	5.21
NCNF-850	90.42	5.54	4.04
NCNF-900	92.36	4.43	3.21

The as-produced NCNFs with high nitrogen content and porous structure may generate more active sites for the oxidation of NO, the breakthrough curves of NOx over NCNFs at room temperature are illustrated in Fig.4. The breakthrough time of NO over

these NCNFs was 1~2 hours, which was longer than that over PCNFs^[19] activated by steam. The increase of breakthrough time is contributed to the introduction of heteroatom (N) in the carbon nanofibers, because it leads to weak chemisorption activities of nanofibers that enhance the micropore filling capability on NO^[11]. After breakthrough, the outlet NO concentration rose to 9, 12 and 10 ppm over NCNF-800, NCNF-850 and NCNF-900 until it arrived at the steady-state concentration. After around 80 hours, NO₂ breakthrough occurred, NO concentration reached maximum level. When NO₂ outlet concentration began to rise, NO outlet concentration started to decrease correspondingly until it reached the steady-state concentration of 7.1, 9.8 and 7.8 ppm over these NCNFs. After 1-2 hours, the outlet concentration of NO rose sharply, which indicated that the process of NO physical adsorption and desorption is slower compared with the following steps. Furthermore, as the NO₂ starts to breakthrough, new vacant active sites will be released for NO adsorption, thus there will be a gradual decrease for NO outlet concentration before it reached the steady-state level. In this time duration, desorption of NO₂ is the rate-limiting step, the role of NCNFs in the present context is of catalyst and the NCNFs sites are continually recovered by desorption of NO₂ from NCNF surface.

Fig.4 Breakthrough curves of NOx over porous nitrogen-doped carbon nanofibers

(a) NCNF-800 (b) NCNF-850 (c) NCNF-900

The breakthrough characteristics of NO_x over NCNFs can be explained using Langmuir-Hinshelwood mechanism ^[1], a preferred heterogeneous catalysis model. In the model, NO and O₂ are firstly adsorbed on the vacant active sites of NCNFs, then NO was oxidized into adsorbed NO₂ (C-NO₂). The C-NO₂ may further react and produce some intermediates, for example, NO₃ and NO-NO₃ that also are adsorbed on the surface of NCNFs. This process can be verified by the change of N1s XPS spectra of NCNFs, the XPS spectra of nitrogen groups (N1s) on NCNF10-850 after adsorption of NO/O₂. Compared the N1s XPS spectra of before and after adsorption of NO/O₂, we can find that another new broad peak was observed clearly that was the overlap of two peaks located at 405.9 and 407.2 eV after adsorption of NO/O₂, they were attributed to -NO₂, -NO₃ group^[33]. Furthermore, the two peaks at 398 and 401 eV shift toward right, their relative strength also changed prominently, the peak at 398 eV was weakened while the peak at 401 eV was enhanced indicating the increase of the relative amount of pyrrole functional groups. This confirmed that the adsorbed NO was oxidized into NO₂ over NCNFs in the presence of O₂, because the shift toward higher binding energy of chemical shift results from the increase of oxidation state for element. At last, the adsorbed intermediate is decomposed into NO₂ from the surface followed by releasing the vacant sites for the subsequent adsorption of successive NO and O₂. Based on the mechanism, during the initial period, the outlet concentration of NO was zero because NO can be completely adsorbed by micropores in NCNFs via physical adsorption, in which NCNFs play the role of adsorbents.

Fig.5 Deconvoluted XPS spectra of nitrogen groups (N1s) on NCNF10-850 after adsorption of NO/O₂

The calculated NO removal efficiency according to equation (1) was 64.5, 51.0 and 61.5 % over NCNF-800, NCNF-850 and NCNF-900, which was much higher than that on PCNFs activated by steam ^[19]. The high NO removal efficiency over NCNFs was mainly due to the enhanced catalytic oxidation activity by nitrogen atoms, since the insertion of nitrogen atoms into the graphite lattice lower the band gap, which leads to produce higher electron mobility and lower the electron work function on the carbon-gas interface ^[34], so the catalytic properties can be improved drastically. Besides the introduction of nitrogen atoms, the textural structures including surface area and micropore volume has prominent effects on the catalytic oxidation efficiency of NCNFs. Therefore, the catalytic activity of NCNF-850 is the lowest among the three NCNFs, for NCNF-850 has medium nitrogen content and micropore volume. It is easily seen that the outlet NO_x concentration over NCNFs are far below the inlet NO_x concentration shown in Fig.4, the decrease of NO_x concentrations is possibly attributed to the reduction of NO into N₂ at the aid of abundant nitrogen functional group in NCNFs.

4. Conclusions

Nitrogen-doped carbon nanofibers (NCNFs) by NH_3 -activation demonstrated high NO removal efficiency. A maximum of 64.5% removal efficiency was acquired at NO initial concentration of 20 ppm and 21 vol% of O_2 at room temperature. Therefore, nitrogen-doped porous carbon nanofibers is an effective and promising materials to be used for NO removal.

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