Activated carbon fibers loaded with MnO₂ for removing NO at room temperature

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ABSTRACT

MnO₂ loaded on activated carbon fibers (MnO₂@ACF) were successfully prepared using co-precipitation methods, the as-prepared MnO₂@ACF were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and N₂ adsorption/desorption analysis. The results showed that MnO₂ particles were highly dispersed with a strong interaction between MnO₂ particles and ACFs. MnO₂ loaded on ACF can promote the catalytic oxidation efficiency of NO into NO₂ remarkably, the loaded amount of MnO₂ has an obvious effect on the NO oxidation efficiency over MnO₂@ACF. The optimal amount of MnO₂ for MnO₂@ACF is 3.64 wt%, and the oxidation efficiency of NO was increased from 20.1% over A15 to 30.6% over MnO₂@ACF.

KEY WORDS: activated carbon fiber; catalytic oxidation; NO removal

1. Introduction

Nitrogen oxides (NO_x) emitted from mobile vehicles and stationary sources are severe harmful atmospheric pollutants for humanity and ecosystem because they can induce acid rain, photochemical smog, and ozone depletion ^[1, 2], so NO_x removal has been the subject of very intense research in the recent years. Among all the NO_x, NO is considered to be the most abundant NO_x contaminants and the most difficult to be removed from ambient air, because NO is nearly insoluble in water as a kind of colorless and odorless gas, while NO₂ is relatively easy to be removed owing to its good dissolving nature in water. Thus, the focus and difficulty of NO_x removal is NO elimination.

Up to now, the extensively studied method of NO removal is selective catalytic reduction (SCR) of NO with ammonia^[3-5], V-based catalysts V₂O₅-WO₃/TiO₂^[6] are used as a common catalyst in the NH₃-SCR process, which shows high catalytic activity and selectivity. However, some inevitable problems exist in the process of NH₃-SCR, such as the high working temperature, the toxicity of vanadium-species^[7] and low N₂ selectivity in high temperature range. Moreover, NH₃-SCR is appropriate to high concentration NO but low efficiency on low concentration, thus NH₃-SCR is generally employed to remove high concentration NO at high temperature from stationary source. Therefore, it is urgent to develop applicable materials or catalysts that can remove low-concentration NO effectively at room temperature.

Another route for removing NO is oxidizing NO into NO₂, which has attracted considerable interests because it can proceed in air at room temperature thermally over some catalysts^[8], the produced NO₂ is captured by basic water as nitrate. Nevertheless, NO is readily to be oxidized into NO₂ by O₂ in the case of high concentration without catalyst even at room

temperature, while it is extremely difficult to transform into NO₂ at low concentration the dynamic limit of NO oxidation^[9]. Carbonaceous materials, such as activated carbon^[10-12], activated carbon fibers (ACF)^[13-15], carbon nanofibers (CNF)^[16, 17] and carbon xerogels^[18] have been proved as effective catalysts of NO oxidation at room temperature, because carbonaceous materials possess many desirable properties, low cost, resistance to acid and base, large surface area and developed pore structure, and high catalytic activity. Most researches related to NO removal by carbonaceous materials have been summarized in the recent review^[19].

Previously, we investigated the catalytic oxidation of low concentration (20 ppm) NO into NO₂ over activated carbon nanofibers (ACNFs) at room temperature, the results show that NO can be effectively oxidized into NO₂ even at low concentration^[16], and the oxidation efficiency can be further increased when graphitized carbon nanofibers were used as catalysts^[17]. Although ACNFs possess excellent catalytic activity for NO oxidation at room temperature, it is not feasible currently to remove NO using ACNFs as catalysts on a large scale due to their high costs. The most promising materials used widely to remove NO at room temperature may be ACFs, some researches on NO oxidation using ACFs as catalysts have been conducted at room temperature^[20-22], but most of these studies focused on high-concentration NO (>400 ppm) oxidation. In our previous work, we investigated the catalytic oxidation of low concentration NO of 50 ppm over pitch-based ACFs at 30 °C^[23], and found that ACFs can catalytically oxide NO into NO₂ in the case of low concentration (50ppm) at room temperature.

To further enhance the catalytic activity of NO oxidation over ACFs, loading some suitable catalysts on ACFs is an available choice. Many transition metal oxide catalysts, such as cerium oxide (CeO₂)^[24, 25], titanium dioxide (TiO₂)^[26, 27], cobalt oxide(Co₃O₄)^[28], especially

manganese oxides (MnO_x)^[29, 30] are effective in NO oxidation process. Here, MnO_2 were co-precipitated onto ACFs and the effects of MnO_2 loading on the catalytic activity of NO oxidation were investigated. It was expected that loading MnO_2 would enhance the oxidation activity of ACFs against NO at room temperature.

2. Experimental

2.1 Materials preparation

Pitch based ACF (A15) was supplied by Osaka Gas Co., Ltd. The ACF sample was dried at 110 °C for 12 hours in vacuum drying oven. Other reagents such as $\text{Mn}(\text{NO}_3)_2$, KMnO_4 , are all analytically pure (AR) reagents and purchased from Beijing Modern Fine Chemical Co., Ltd.

The process of co-precipitation for loading manganese oxide on ACF was as follows: ACF was firstly dipped into manganous nitrate ($\text{Mn}(\text{NO}_3)_2$) solution, then potassium permanganate (KMnO_4) solution was added under violent stirring, redox reaction occurred between KMnO_4 and $\text{Mn}(\text{NO}_3)_2$ which resulted in manganese oxide depositing in the surface and pores of ACF. Adjusting the concentrations of $\text{Mn}(\text{NO}_3)_2$ and KMnO_4 , MnO_2 -loaded ACF ($\text{MnO}_2@\text{ACF}$) with controllable MnO_2 loading amount can be obtained. Here, various concentrations (0.005~0.05 mol/L) of KMnO_4 and $\text{Mn}(\text{NO}_3)_2$ were used, ACF sample was firstly soaked in $\text{Mn}(\text{NO}_3)_2$ solution for one hour, then KMnO_4 solution was dropwise added under violent stirring. After the solution containing ACF was stirred continuously for 90min, the ACF was taken out of the solution and dried at 120 °C for 4 hours in vacuum drying oven. Finally, the dried ACF was heat treated at 200 °C for 2 h under N_2 . The MnO_2 content was determined by the mass difference between the pristine ACFs and the ACFs loaded with MnO_2 .

2.2 Characterization

The morphologies of ACF samples were observed by a field emission scanning electron microscope (SEM, LEO-1530). Powder X-ray diffraction (XRD) was performed with a D8 advance X-ray diffractometer using nickel filtered Cu-K α (40 kV, 30 mA) radiation and a secondary beam graphite monochromator. The samples were scanned at a rate of 4 °/min over the range of $5^{\circ} \leq 2\theta \leq 90^{\circ}$. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific ESCALAB 250Xi system equipped with a dual X-ray source using Al-K α . All the binding energies were calibrated using contaminant carbon (C1s=284.6 eV) as a reference, the chemical state of all substances are determined according to Handbook of X-ray photoelectron spectroscopy (Chastain J, 1992).

Nitrogen adsorption-desorption isotherms of all samples were measured in volumetric adsorption systems (BELSORP-max, Bel, Japan) at 77K. Before the measurements, all the samples were degassed at 200 °C for 12 hours. The specific surface area of samples was calculated by α_s method^[31], because α_s is more suitable to evaluating the surface area of samples that show typical I-type adsorption-desorption isotherms. The pore volume and pore size distribution of samples were calculated by applying the quenched solid density functional theory (QSDFT)^[32] to the nitrogen isotherms.

Temperature-programmed desorption (TPD) experiments of NO/O₂ were conducted on a Chem BET Pulsar chemisorption analyzer (Quantachrome Instruments, USA). In the NO-TPD experiments, about 20 mg sample was used and firstly outgassed at 200 °C in He atmosphere (100 ml/min) for 1h, then cooled to 50 °C. After NO/O₂ (60 SCCM) was passed through the sample for 60 min, the sample was flushed with He at the same temperature for 30 min. Finally, the sample was subsequently subjected to TPD under He flow, the TPD operation was carried

out from 50 to 1000 °C at a ramping rate of 10 °C /min, and the He flow was 100 SCCM. The evolved gases were monitored by a thermal conductivity detector (TCD).

2.3 Catalytic activity measurements

The catalytic oxidation activity measurement of MnO₂@ACF was carried out in a fixed-bed quartz micro-reactor (ϕ 11mm × 50 mm) operating in a steady state flow mode, 100 mg of the sample was used in each test and the packing length of sample in reactor was 6 mm. The reactant gas consists of 50 ppm NO, 21 vol.% O₂ with balance N₂, the total flow rate were adjusted to 200 SCCM by mass flow control system. The temperature was monitored at 30 °C with a thermostatic water bath through dipping the reactor in the water bath, the concentration of NO_x in the inlet and outlet gas was measured by a NO_x chemiluminescence analyzer of NO-NO₂-NO_x (Thermo Electron Co., USA, model 42i).

3. Results and discussion

3.1 Characteristics of MnO₂@ACF

As described in 2.1, MnO₂ was loaded on ACFs in-situ by co-precipitation method, MnO₂ was produced by the following reactions:

The co-precipitation method is an effective way to synthesize MnO₂ nanoparticles, high purity MnO₂ nanoparticles can be obtained, and as-produced precipitants are MnO₂, which is confirmed by the XRD patterns (Fig.1). Obviously, the amount of KMnO₄ and Mn(NO₃)₂ determine the amount of MnO₂, different amount of MnO₂ can be loaded onto ACF by adjusting the concentration of KMnO₄ and Mn(NO₃)₂, the results are listed in Table 1, the loading amount of MnO₂ increased with increase of concentrations of the Mn sources.

Table 1 Loading amount of MnO₂ on A15 under different concentrations

Conc. of KMnO ₄	Conc. of Mn(NO ₃) ₂	Loading amount of MnO ₂
(mol/L)	(mol/L)	on A15 (wt %)
0.005	0.005	0.61
0.01	0.01	1.83
0.02	0.02	2.63
0.03	0.03	3.64
0.04	0.04	4.26
0.05	0.05	5.07

The XRD patterns of MnO₂ powder and MnO₂@ACFs prepared by co-precipitation are shown in Figure 1. It can be seen that the MnO₂ obtained was mainly γ -MnO₂ because the XRD pattern of powder MnO₂ had obvious peaks at 23.03, 37.01, 42.39, 56.03, 66.13°, respectively, which agree well with the identification cards of γ -MnO₂ (JCPD#97-002-0228). The ACF and MnO₂@ACF samples have two broad peaks at about 25° and 43°, which can be assigned to the reflection of planes (002), and the overlapped reflection of planes (100) and (101), respectively. The encapsulation of MnO₂ did not change the XRD patterns of ACFs, because the MnO₂ loaded amount was too small for the maximum amount of MnO₂ was just 5.07 wt%.

Fig.1 XRD patterns of A15, MnO₂ and MnO₂@A15

The fine particles and aggregated MnO₂ particles were observed on the surfaces of activated carbon fiber (A15) as indicated in Figure 2. As shown in this figure, the surface of the unmodified carbon fiber (Fig.2a) is smooth and clean. Figure 2b, 2c and 2d show the activated carbon fibers loaded with MnO₂ which represented the amount of 1.83, 2.63 and 3.64 wt.%, respectively. The small particles, sparsely attached to the fiber surface, were produced from MnO₂ precipitation in solution. It is obvious that the particles became dense with the increase of the concentration of MnO₂ sources.

Fig.2 SEM images of unmodified activated carbon fiber A15(a), $\text{MnO}_2\text{-1.83\%@A15}$, $\text{MnO}_2\text{-2.63\%@A15}$ and $\text{MnO}_2\text{-3.64\%@A15}$

Nitrogen adsorption isotherms at 77 K of A15, $\text{MnO}_2\text{-1.83\%@A15}$ and $\text{MnO}_2\text{-3.64\%@A15}$ are presented in Fig. 3(a). All of them exhibit a type I adsorption isotherm according to the IUPAC classification^[33], which indicated that all samples were microporous materials. Obviously, the adsorption amount of A15 loaded with MnO_2 decreased markedly, which were contributed to the MnO_2 particles covering the surface and blocking the pores of A15. Based on the nitrogen adsorption isotherms, the calculated α_s surface area of the three samples is 1890, 805, 718 m^2/g , respectively. The pore volume evaluated via QSDFT for the samples is 0.794, 0.306 and 0.289 cm^3/g , and the pore size distribution was illustrated in Fig. 3(b), which show clearly the pores are almost micropores, and the pore volume decreased with the loaded amount

of MnO₂ particles.

Fig.3 N₂ adsorption–desorption isotherms obtained at 77 K (a) and derived micropore size distribution (b) for A15, MnO₂-1.83%@A15 and MnO₂-3.64%@A15

3.2 Effect of MnO₂ on catalytic oxidation of ACF against NO

Fig.4 illustrates the time course of NO oxidation into NO₂ at room temperature on A15 and MnO₂@A15, where NO and O₂ concentrations were 50 ppm and 21 vol.% in N₂, respectively. The samples, A15, MnO₂-0.61%@A15, MnO₂-1.83%@A15, MnO₂-2.63%@A15, MnO₂-3.64%@A15, MnO₂-4.26%@A15 and MnO₂-5.07%@A15 were used as catalysts for NO oxidation. As shown in Fig. 4, NO broke through over 0.1 g A15 sample soon after the reaction gas flow, and its outlet concentration increased rapidly within the initial 2 hours, which reveals that it is difficult to remove NO only by adsorption. Later, the NO outlet concentration continued to increase its maximum (45 ppm) until NO₂ appeared in the outlet gas. When NO₂ concentration rose to its maximum value, the NO concentration decreased to a stationary level.

Fig.4 Time course of NO oxidation over A15 and MnO₂@A15 with different loading amount of MnO₂. NO: 50 ppm (N₂ balance) inlet, Temp.=30 °C, RH: 0 %, sample weight: 0.1 g.

Mn-based catalysts have been intensively studied as catalysts for low temperature NH₃-SCR^[34], but few investigations on the oxidation of NO at room temperature. Here, MnO₂ was used as catalysts to oxidize NO into NO₂ over ACF. In order to investigate the effect of MnO₂ on the NO oxidation over ACF, six samples with different amount of MnO₂ on A15 were tested. Compared with A15, the A15 loaded with MnO₂ show distinct performance in the course of NO oxidation. The significant difference between A15 and modified A15 is that the outlet NO₂ at stationary state had remarkable different concentrations. It is seen from Fig.4 that the NO₂ outlet concentration over A15 at stationary state is about 10 ppm, which is the lowest one over all the samples. The highest NO₂ outlet concentration at stationary state is 15.4 ppm over MnO₂-3.64%@A15 at room temperature. The NO₂ outlet concentration over other modified A15 is higher than that of A15. To elucidate the NO oxidation effect over these samples, the catalytic oxidation efficiency of NO (η) can be defined as follows:

$$\eta = \frac{C_1}{C_1 + C_2} \times 100\% \quad (2)$$

Where, C_1 represents the concentration of NO_2 at the stationary stage, C_2 represents the concentration of NO at the stationary stage. In this case, the sum of C_1 and C_2 is equal to 50 ppm, which indicates that NO can be oxidized other than reduced over ACF. On the basis of formula (2) and the data shown in Fig.4, the calculated oxidation of efficiency of these samples is presented in Fig.5.

Fig.5 NO oxidation efficiency with MnO_2 loading amount on A15

When the loading amount of MnO_2 increased from 0 to 3.64 %, η correspondingly increased from 20.1 to 30.6 %. But as the MnO_2 content continuously rose to 4.26 and 5.07 %, the oxidation efficiency declined on the contrary, which illustrated that there is an optimal MnO_2 loading amount on A15 for the NO oxidation at room temperature. In contrast with unmodified A15, the oxidation capability of A15 loaded with MnO_2 can be improved by 50 % at the same conditions, we can conclude that MnO_2 plays a vital role during the catalytic oxidation of NO . Although 44-75% NO can be converted into NO_2 on pitch-based ACF at room temperature^[10], much more

amount of ACF (0.4g) were used and the initial NO concentration (400 ppm) was high with a low total gas flow (100 SCCM), while 0.1 g ACF was used and the initial NO concentration was 50 ppm with a total gas flow of 200 SCCM in this study. Generally, NO conversion efficiency is increased at a high initial NO concentration under a low gas flow rate using more ACFs. Moreover, such a capability can be enhanced by using graphitized porous carbon^[17], but the graphitization is energy-consuming. Therefore, the promising and effective materials are modified ACFs by loading some catalysts. It is noted that the oxidation efficiency decreased and NO₂ breakthrough time shortened at a higher loading amount due to the surface covering, pore blocking and the aggregation of MnO₂ particles. Hence, too much MnO₂ was not helpful for the catalytic oxidation of NO, the loading MnO₂ should be controlled at an optimal amount.

XPS experiments were conducted to investigate the surface electronic state of the MnO₂@A15 catalysts, and the results are illustrated in Fig.6. Here, the “after test” meant that the sample was used as catalysts for catalytically oxidizing NO and the “before test” represented as-prepared MnO₂@A15. Two main peaks responding to Mn 2p_{1/2} and Mn 2p_{3/2} appeared in the Mn 2p spectra for the both MnO₂@A15 samples before and after testing. The two peaks located at 643.5 and 655.4 eV, which agree well with that of the standard binding energies of MnO₂^[35]. Comparing the spectra of before with the after-test samples, it is observed that the corresponding peaks became broad and the location of peaks shifted for the “after test” samples, which indicated that MnO₂ acted as catalysts in the oxidation process of NO. According to the postulated reaction mechanism^[13], NO is firstly adsorbed on the active sites of ACF, then oxidized to NO₂ in the presence of O₂, the oxidation process is enhanced by MnO₂. The as-produced NO₂ may react and yield some intermediates, such as NO₃ and NO–NO₃ in adsorbed phase. ACF acted both as

catalyst and adsorbent, MnO_2 facilitates the catalytic oxidation of NO into NO_2 .

Fig.6 Mn2p XPS spectra of $\text{MnO}_2@\text{A15}$ before test and after test

Temperature programmed desorption (TPD) is an effective approach determining the surface chemical species of catalysts, the NO/O_2 -TPD profiles of A15 and $\text{MnO}_2@\text{A15}$ are presented in Fig.7. For unloaded A15, there is one strong desorption peak about 140°C and several weak desorption peaks at 294°C , 710°C and 812°C . The peak at 140°C is attributed to the desorption of $\text{NO}^{[36]}$, which implied that NO can be adsorbed on the surface of activated carbon fibers by acid-base interactions. Compared with A15, the NO/O_2 -TPD on $\text{MnO}_2@\text{A15}$, there was great difference, the strong desorption peak of NO shifted left to 120°C , the desorption peak at 294°C while a broad desorption peak about 432°C was observed. Based on these, the peak about 432°C may come from the desorption of NO on the MnO_2 sites, which indicated that loaded MnO_2 can provide more adsorption sites of NO and enhance the adsorption capability of NO on A15. The TPD results agree well with XPS characterization.

Fig.7 TPD profiles of A15 and MnO₂@A15

4. Conclusions

Activated carbon fibers (ACF) loaded with MnO₂ were successfully prepared by co-precipitation, and MnO₂@ACF were used for catalytic removal low-concentration NO of 50 ppm at room temperature. The MnO₂ loaded on ACF can promote the catalytic oxidation efficiency of NO into NO₂ remarkably. The loaded amount of MnO₂ has a prominent effect on the NO oxidation efficiency, the optimal amount for MnO₂@A15 is 3.64 wt%, and the oxidation efficiency of NO increased from 20.1 % over A15 to 30.6 % over MnO₂-3.64%@A15. It suggests that the activated carbon fibers loaded with MnO₂ would be promising materials for removing NO_x at room temperature.

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