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Activated carbon fibers loaded with MnO_2 for removing NO at room temperature

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HIGHLIGHTS

- We prepared MnO_2-loaded activated carbon fibers by co-precipitation method.
- MnO_2 loading can remarkably promote ACF's catalytic oxidation efficiency for NO.
- The NO removal efficiency of MnO_2/ACF composite depends on the MnO_2 loaded amount.

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ABSTRACT

MnO_2 loaded on activated carbon fibers (MnO_2@ACF) were successfully prepared using co-precipitation methods, the as-prepared MnO_2@ACF were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and N_2 adsorption/desorption analysis. The results showed that MnO_2 particles were highly dispersed with a strong interaction between MnO_2 particles and ACFs. MnO_2 loaded on ACF can promote the catalytic oxidation efficiency of NO into NO_2 remarkably, the loaded amount of MnO_2 has an obvious effect on the NO oxidation efficiency over MnO_2@ACF. The optimal amount of MnO_2 for MnO_2@ACF is 3.64 wt.%, and the oxidation efficiency of NO was increased from 20.1% over A15 to 30.6% over MnO_2@ACF.

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 NO_2 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 V_2O_5-WO_3/TiO_2 [6] are used as a common catalyst in the NH_3-SCR process, which shows high catalytic activity and selectivity. However, some inevitable problems exist in the process of NH_3-SCR, such as the high working temperature, the toxicity of vanadium-species [7] and low N_2 selectivity in high temperature range. Moreover, NH_3-SCR is appropriate to high concentration NO but low efficiency on low concentration, thus NH_3-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 NO_2, which has attracted considerable interests because it can proceed in air at room temperature thermally over some catalysts [8], the produced NO_2 is captured by basic water as nitrate. Nevertheless, NO is readily to be oxidized into NO_2 by O_2 in the case of high concentration without catalyst even at room temperature, while it is extremely difficult to transform into NO_2 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

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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 NO_2 over activated carbon nanofibers (ACNFs) at room temperature, the results show that NO can be effectively oxidized into NO_2 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 NO_2 in the case of low concentration (50 ppm) 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 (CeO_2) [24,25], titanium dioxide (TiO_2) [26,27], cobalt oxide (Co_3O_4) [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 h in vacuum drying oven. Other reagents such as $Mn(NO_3)_2$, $KMnO_4$, 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 ($Mn(NO_3)_2$) solution, then potassium permanganate ($KMnO_4$) solution was added under violent stirring, redox reaction occurred between $KMnO_4$ and $Mn(NO_3)_2$ which resulted in manganese oxide depositing in the surface and pores of ACF. Adjusting the concentrations of $Mn(NO_3)_2$ and $KMnO_4$, MnO_2-loaded ACF (MnO_2@ACF) with controllable MnO_2 loading amount can be obtained. Here, various concentrations (0.005~0.05 mol/L) of $KMnO_4$ and $Mn(NO_3)_2$ were used, ACF sample was firstly soaked in $Mn(NO_3)_2$ solution for 1 h, then $KMnO_4$ solution was dropwise added under violent stirring. After the solution containing ACF was stirred continuously for 90 min, the ACF was taken out of the solution and dried at 120 °C for 4 h 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-Kα (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 $5° \leqslant 2\theta \leqslant 90°$. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific ESCALAB 250Xi system equipped with a dual X-ray source using Al-Kα. 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 77 K. Before the measurements, all the samples were degassed at 200 °C for 12 h. 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/O_2 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 1 h, then cooled to 50 °C. After NO/O_2 (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 MnO_2@ACF was carried out in a fixed-bed quartz micro-reactor (ϕ 11 mm × 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.% O_2 with balance N_2, 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–NO_2–NO_x (Thermo Electron Co., USA, model 42i).

3. Results and discussion

3.1. Characteristics of MnO_2@ACF

As described in Section 2.1, MnO_2 was loaded on ACFs in-situ by co-precipitation method, MnO_2 was produced by the following reactions:

$$3Mn(NO_3)_2 + 2KMnO_4 + 2H_2O = 5MnO_2 + 2KNO_3 + 4HNO_3 \qquad (1)$$

The co-precipitation method is an effective way to synthesize MnO_2 nanoparticles, high purity MnO_2 nanoparticles can be obtained, and as-produced precipitants are MnO_2, which is confirmed by the XRD patterns (Fig. 1). Obviously, the amount of $KMnO_4$ and $Mn(NO_3)_2$ determine the amount of MnO_2, different amount of MnO_2 can be loaded onto ACF by adjusting the concentration of $KMnO_4$ and $Mn(NO_3)_2$, the results are listed in Table 1, the loading amount of MnO_2 increased with increase of concentrations of the Mn sources.

The XRD patterns of MnO_2 powder and MnO_2@ACFs prepared by co-precipitation are shown in Fig. 1. It can be seen that the