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NO adsorption on activated carbon fibers from iron-containing pitch

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Abstract

Iron-containing activated carbon fibers (Fe-ACF) have been prepared by a novel method consisting of mixing an iron precursor with raw pitch before carbon fiber formation, and further CO_2 activation of the Fe-CF. The NO adsorption experiment revealed that iron species are accessible to gases and that they activate NO improving adsorption into the fiber microporosity. The chemisorption of NO and the subsequent dimer (N_2O_2) formation is, in general, the rate-limiting step. Metallic iron and/or partially reduced iron compounds are the most active iron species. However, in the fibers with narrow micropores dimer diffusion in the microporosity is the slowest step and, consequently, an appropriate pore size is required from a kinetic point of view. The most suitable samples prepared were those with pores wider than 0.7 nm which contain partially reduced iron species. Finally, NO adsorbed can be further recovered by heating the spent adsorbents at a quite low temperature (500 K). Fresh and regenerated adsorbents show similar NO adsorption capacity.

Keywords: Microporosity; NO adsorption; Thermal analysis

1. Introduction

Activated carbon fibers (ACF) are promising solid adsorbents since they present very interesting performance in comparison to conventional activated carbons (AC). The porous texture of ACF has been object of great attention. These materials are essentially microporous [1,2], being very suitable for gas-pollution control applications [3,4]. AC materials are receiving special attention due to their unique properties for adsorption of atmospheric pollutants, such as nitrogen oxides (NO_x). Different NO_x abatement processes have been proposed, AC being useful either as catalyst support or as solid reactant for NO_x reduction to N_2, avoiding reductant slip [5–7]. ACF can be also used in the former process but not in the latter due to the high price of ACF manufacturing, since carbon is consumed in the process. In addition, reversible NO adsorption on microporous carbon materials has been proposed. This approach presents the advantage of NO recovery, which is further used in the synthesis of valuable products. Several studies have been reported dealing with ACF utilization for this application, ACF presenting the best performance among the different porous materials studied due to their unique microporous network [8–10]. However, NO is a supercritical gas under ambient conditions, and low NO adsorption values are reached. It has been reported that NO adsorption is improved by chemisorption on suitable metals, with iron oxides showing a high activity [11]. Different iron-impregnated ACF synthesis methods, involving several steps, were checked by Kaneko et al. [12–14]. With these methods a very promising NO adsorption capacity (320 mgNO/gC at 80 kPa and 303 K), under highly concentrated NO streams, were achieved.

NO removal at room temperature, and from low NO concentration, is desirable in many applications, such as, diluted NO removal in highway tunnels or in enclose parking areas. In this case, high NO adsorption capacity

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is necessary along with rapid adsorption kinetics. On the other hand, simple manufacturing procedures are desirable for the adsorbent preparation.

In a recent article [15], the preparation of iron-containing ACF (Fe-ACF) was studied. An iron precursor was added to the raw pitch selected for Fe-CF preparation. 0.1 wt% of iron was observed to enhance drastically the activation by CO_2 of the Fe-CF samples, also affecting the porosity of the resulting Fe-ACF.

In the current study, Fe-ACFs have been studied for NO adsorption at room temperature, analyzing the activity of the different iron species formed upon the synthesis. Iron exposure to the gas is crucial for this application and it is evaluated, since the fraction of iron located in the carbon bulk is not expected to participate in NO adsorption. The effect of the textural properties of the Fe-ACF on NO adsorption was discussed and, finally, the adsorption kinetics have been analyzed.

2. Experimental

The preparation procedure and characterization results of the Fe-ACF used in this study were described in detail elsewhere [15]. In brief, $FeCl_3$ was carefully mixed with petroleum pitch ($0.001\ gFeCl_3/g_{pitch}$). The iron-containing pitch was spun, and the resulting Fe-CF was stabilized in air at 573 K, carbonized in N_2 at 1173 K, and finally activated under CO_2 flow at 1073 K. The Fe-ACF are denoted by CFe%, % indicating the burn-off in weight percent after the activation step (for example, activated Fe-CF with 8% burn-off is named CFe8).

Table 1 summarizes some of the Fe-ACF characterization results, including the pore volumes as determined by CO_2 (V_c) and N_2 (V_n) adsorption at 273 and 77 K, respectively, using the DR equation, and the different iron species identified by XRD. CO_2 and N_2 adsorption measurements were carried out in an automatic Quantachrome volumetric system (Autosorb-6), and X-ray diffraction patterns were recorded in a 2002 Seifert powder diffractometer. The different pore volumes used in our discussion have been calculated as follows:

- The volume of the narrowest micropores (pore size <0.7 nm), also called ultramicropores, V_c, was estimated from the CO_2 DRs plots (relative pressures <0.015).
- The volume of the total micropores (pore size <2 nm), V_n, was calculated from the N_2 DRs plots (relative pressures <0.14).
- The volume of supermicropores (0.7 nm < pore size <2 nm) is given by the difference V_n–V_c.

Table 1
Fe-ACF pore volumes as determined by N_2 (V_n) and CO_2 (V_c) adsorption and iron species contained in these fibers

	V_n (cm^3/g)	V_c (cm^3/g)	Iron species (XRD)
CFe	0.13	0.15	Fe/C, Fe_3C, Fe
CFe8	0.26	0.24	Fe, FeO
CFe25	0.36	0.31	FeO, Fe_3O_4
CFe38	0.43	0.20	Fe_3O_4, Fe_2O_3
CFe50	0.46	0.25	Fe_2O_3

V_n: pore volume determined by N_2 adsorption at 77 K; V_c: pore volume determined by CO_2 adsorption at 273 K.

NO adsorption on Fe-ACF was studied in a Stanton Redcroft thermobalance (STA-780), with ±10 μg accuracy. Twenty milligram of sample was used for each run. The sample was treated at 373 K under He and, after weight stabilization, the temperature was decreased and maintained at the adsorption temperature (300 K). 60 ml/min of 5%NO and He balance was used in the adsorption step, which was conducted for 4 h. The weight increase during adsorption was corrected with that measured in a blank experiment. After the adsorption step, the NO/He mixture was replaced by He, and the temperature was raised at 10 K/min up to 473 K (regeneration) or 1223 K (heat treatment). NO was removed during these treatments and the NO adsorption capacity of the Fe-ACF samples (either regenerated at 473 K or heat-treated at 1223 K) was further determined under similar adsorption conditions to those used for the first adsorption step (300 K; 60 ml/min of 5%NO/He). The nomenclature of the samples includes the term "r" and "t" to indicate the "regenerated" and "heat-treated samples", respectively.

In addition, the process consisted of NO adsorption at 300 K and posterior thermally treatment at 1223 K was also carried out with selected samples in a fixed-bed reactor coupled to a chemiluminiscence NO_x analyser (Thermo Environmental Model 42H) and a gas chromatograph (Hewlett Packard, Model 5892A) for gas decomposition monitoring.

3. Results and discussion

3.1. NO adsorption on Fe-ACF

3.1.1. NO adsorption capacity

Fig. 1 compiles the NO adsorption curves obtained at 300 K with Fe-ACF under 5%NO/He. In agreement with

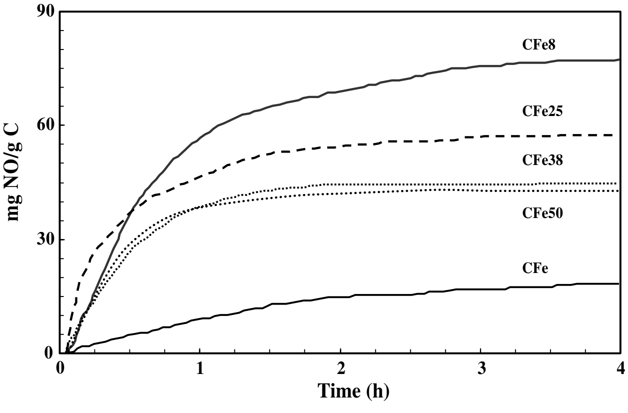

Fig. 1. NO adsorption curves obtained at 300 K for Fe-ACF.