



Activated carbon fibers modified by metal oxide as effective structured adsorbents for acetaldehyde



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ABSTRACT

Novel efficient adsorbents for acetaldehyde removal from diluted gas streams (~1300 ppmv) have been developed. The adsorbents combine the properties of activated carbon fibers (ACF) and nanoparticles (NPs) of basic metal oxides (La_2O_3 , CaO, MgO, ZnO, Al_2O_3). The adsorbents have been prepared by wetness impregnation of ACF using different precursors. The NPs are well dispersed and have average particle size below 2 nm. The ACFs-based adsorbents have an open regular macrostructure with low resistance to gas-flow (low pressure drop) and allow fast adsorption without any diffusion resistance. The NPs deposition provides up to 10-fold increase of acetaldehyde amount adsorbed as compared to non-modified ACF. The adsorption capacity increased with the basicity of metal oxides attaining 20 wt.% on $\text{La}_2\text{O}_3/\text{ACF}$. The materials are characterized by different techniques including temperature-programmed desorption (TPD) and high resolution scanning transmission electron microscopy (HRSTEM).

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1. Introduction

Volatile organic compounds (VOC) are pollutants often encountered in industrial gas emissions. Due to their toxicity and their impact on the environment even at low concentrations [1,2], their release is subjected to legal limits [3]. Therefore, development of new VOC adsorbents has become of a great interest during the last decades [4].

Several methods, such as condensation [5], thermal oxidation [6], absorption [7] and bio-filtration [8,9] are commonly used for VOC abatement from gas streams. All of them are efficient at relatively high VOC concentrations (>5000 ppmv) [10]. However, industrial flue gas streams are often highly diluted, and the development of efficient methods to treat such mixtures is still of great importance. Among the known methods, adsorption shows the best results in terms of efficiency, energy costs and versatility to different compounds [11]. Various adsorbents are used for VOC abatement such as activated carbon [2], zeolites [12,13], polymers [14] or silica [15]. Due to its low costs, activated carbon is often used at industrial scale [10] usually in the form of pellet or granules [16]. Activated carbon fiber (ACF) materials (tissue, felt, etc.), consisting of arranged microfilaments represent a

valuable alternative to randomly packed beds of granulated carbons. ACFs present important advantages due to a high specific surface area, low pressure drop and suppressed mass transfer limitations [17,18].

Many studies devoted to the removal of non-polar low-concentrated VOC, such as benzene, toluene and other hydrocarbons, by adsorption on different types of activated carbon have been published [2,16,19–21]. Large adsorption capacities are usually reported. However, the information concerning the adsorption of oxygenated VOC on activated carbons is still scarce in the open literature.

Oxygenated VOC, such as alcohols, aldehydes, etc., are normally adsorbed on carbon surface via hydrogen bonding with O-containing groups. Since activated carbons usually contain only a small amount of oxygen, the increase of their adsorption capacity toward oxygenated VOC is achieved by oxidizing the carbon surface. Nitric acid is an example of oxidizing agents leading to an increase of the carbon adsorption capacity [22–24]. Another approach to increase the adsorption capacity toward VOC consists in introducing N-containing groups via a gaseous ammonia treatment [22]. However, at low concentrations of oxygenated VOC the uptake by modified activated carbons remains quite low. Recently, nanocrystalline aerogels of metal oxides were proposed as effective adsorbents for a variety of oxygenated VOC. The adsorption capacity of these materials was found to be larger as compared to activated carbons due to a multilayer dissociative adsorption of VOC [25].

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The goal of the present work was to develop novel ACF based structured adsorbents for efficient removal of oxygenated VOC from low-concentrated streams. Our approach is based on a conjugation of ACF properties (large surface area and open macrostructure) with the reactivity of metal oxide NPs. The developed adsorbents were tested for acetaldehyde removal taken as a model of oxygenated VOC.

2. Experimental

2.1. Material

Two types of ACFs provided by Kynol Europa GmbH (Hamburg, Germany) were used as starting materials namely ACF-K-10 (SSA $\sim 1000 \text{ m}^2 \text{ g}^{-1}$) and ACF-K-20 (SSA $\sim 2000 \text{ m}^2 \text{ g}^{-1}$). The ACFs are produced from novoloid phenolic precursor fibers by a one step process combining carbonization and chemical activation.

The ACFs were modified by deposition of metal oxide nanoparticles via wetness impregnation of a precursor followed by its thermal decomposition. The used precursors: $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Ti(IV) bis(ammonium lactato)dihydroxide, were all provided by Sigma–Aldrich (>98% purity). In a standard procedure, the fibers were first dipped into a solution of a metal salt in ethanol (>99.8%, Fluka) or water (Ti(IV) bis(ammonium lactato)dihydroxide). The metal salts concentrations were calculated using the ACF wetness capacity to obtain the final metal oxide loading of 5 wt.%. The impregnated fibers were then dried in air and thermally treated in a He flow (50 ml min^{-1}) (temperature ramp – 10 K min^{-1}). The treatment temperature was set higher than the decomposition temperature of the precursor.

HNO_3 treated ACF (ACF-K-20/ HNO_3) were prepared by immersion of original ACF-K-20 in a boiling 15% (v/v) aqueous solution of nitric acid for 45 min followed by a rinsing with demineralized water and dried in ambient air.

All the gases used in this study: He (99.999%) and 0.13% (v/v) acetaldehyde in He were provided by Carbagas.

2.2. Adsorbent characterization

The specific surface area (SSA) and pore size distribution were determined by physical adsorption of N_2 at 77 K using a Sorpomatic 1990 (Carlo Erba Instruments). Prior to analysis, the samples were outgassed at 523 K for 2 h under vacuum ($7 \cdot 10^{-2}$ bar). N_2 adsorption/desorption isotherms were recorded at 77 K over the relative pressure range of $0.0005 \leq p/p^0 \leq 0.98$. The total pore volume and specific surface area were calculated using BET method [26].

Scanning electron microscopy (SEM) was carried out using a Carl Zeiss MERLIN FE-SEM equipped with two, annular and Everhart-Thornley secondary-electron (SE), detectors operated at an accelerating voltage of 5–30 keV with a beam current of 1.0–3.0 nA and using ZeissSmartSEM software for data acquisition/manipulation.

FEI Tecnai Osiris instrument was used for acquiring the scanning transmission electron microscopy (STEM) images. The high angle annular dark field (HAADF) and energy-dispersive X-ray spectroscopy (EDX) detectors were employed. Measurements were carried out at the maximum accelerating voltage of 200 keV. Specimens were prepared by embedding fibers in epoxy resin followed by ultramicrotomy (diamond grade) and eventually deposition on a holey carbon/Cu grid (300 mesh).

2.3. Dynamic adsorption measurements

Before measurements, the ACF samples ($20 \pm 0.1 \text{ mg}$) were placed in the central part of the glass tubular reactor and outgassed at 298 K in a He flow ($40 \text{ cm}^3 \text{ min}^{-1}$). The adsorption experiments were carried out at $298 \pm 1 \text{ K}$ with a gas flow rate of $200 \text{ cm}^3 \text{ min}^{-1}$ (linear velocity – 0.5 m s^{-1}) regulated by mass flow controllers (EL-FLOW, Bronkhorst). The gaseous mixture containing 1300 ppmv of acetaldehyde and Ar tracer (2% v/v) in He was injected within the adsorbent bed to get the response without adsorption. The adsorbent bed downstream analysis was performed with a mass spectrometer (Thermostar, Pfeiffer Vacuum). A monitoring of the Argon signal was carried out systematically to ensure the absence of channeling or preferential path in the adsorbent bed. A piston type flow pattern was obtained.

A standard adsorption capacity measurement consisted of the following steps:

1. Stabilization of an acetaldehyde mixture flow through the bypass for 15 min to measure the inlet acetaldehyde concentration.
2. After a switch to the reactor, the acetaldehyde mixture flowed through the adsorbent bed until the continuously measured outlet acetaldehyde concentration reached its inlet value measured during the stabilization step.

In such a manner a breakthrough curve was obtained. The breakthrough curves were numerically integrated and the adsorption capacities were obtained. The experiments were carried out three times and the values reported are the mean.

2.4. Temperature-programmed desorption (TPD)

TPD of acetaldehyde was carried out in the same setup with the samples saturated by acetaldehyde at 298 K. The adsorbents were then heated in a He flow ($50 \text{ cm}^3 \text{ min}^{-1}$) at different temperature ramps ($3\text{--}30 \text{ K min}^{-1}$). The outlet concentration of desorbed acetaldehyde was continuously monitored by the mass spectrometer (mass 29 and 44) and plotted as a function of temperature to obtain a TPD pattern. The concentration of CO_2 (mass 44 only) was also monitored.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. Morphology

A representative SEM image of the initial ACF-K-20 is shown in Fig. 1. As can be seen, the material consists of $\sim 10 \mu\text{m}$ diameter elementary filaments. Its open macrostructure provides a low pressure drop during gas flow through the adsorbent bed.

The recorded N_2 adsorption isotherms of the original and MgO modified ACFs are shown in Fig. 2. The isotherms correspond to the type I (according to the IUPAC classification) typical for microporous materials (pore diameter <2 nm). The micropores of the original ACF-K-10 are narrower as compared to ACF-K-20, since the flat part of the ACF-K-10 isotherm starts at lower p/p^0 . The specific surface area of the adsorbents was calculated from N_2 adsorption data using the BET equation.

$$\frac{p}{V(p^0 - p)} = \frac{1}{V_m C} + \frac{(C - 1)p}{V_m C p^0} \quad (1)$$

where V is the amount adsorbed (at STP, $\text{cm}^3 \text{ g}^{-1}$), V_m is a monolayer material capacity (at STP, $\text{cm}^3 \text{ g}^{-1}$), and C is an empirical constant which characterizes adsorption energetics. The BET equation was linearized in the pressure range from 0.001 to 0.1.

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