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Removal of methyl–ethyl ketone vapour on polyacrylonitrile-derived carbon/mesoporous silica nanocomposite adsorbents

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ABSTRACT

Mesoporous silica supports (MCM-41, SBA-15 and silica gel) were modified by the introduction of controlled amounts of polymer-derived carbon. Precipitation polymerization of polyacrylonitrile in the aqueous suspension of a silica material was used as a deposition method. The samples of PAN/silica composites were studied by thermal analysis, performed in air and inert atmosphere, in order to determine the amount of a deposited polymer and its thermal stability. The effect of surface area of a silica support and the monomer concentration in the mother solution on the effectiveness of deposition was revealed. The PAN/silica composites were transformed into C/SiO_2 adsorbents by carbonization carried out at 623 K. Texture (low-temperature sorption of N_2), surface structure (FTIR-DRIFT) and morphology (SEM) of the carbonized samples were investigated. The adsorption tests in the elimination of methyl–ethyl ketone from gas phase were performed under dynamic conditions. The MCM-41-based composites containing highly dispersed carbon layers on the surface appeared to be the most promising adsorbents for a commercial application. Moreover, these materials exhibited a high stability in the adsorption–desorption runs repeated ten times suggesting the possibility of regeneration of the adsorbent bed without a significant loss in the adsorption effectiveness.

1. Introduction

Volatile organic compounds (VOCs) are a large-number group of low-boiling liquid organic pollutants, characterized by boiling points in the range 323–533 K under normal atmospheric pressure [1], discharged into the atmosphere. This group includes aliphatic and aromatic hydrocarbons, alcohols, carbonyl compounds as well as various hydrocarbon derivatives containing other elements like halogens, nitrogen and sulphur. VOCs contribute to increasing the greenhouse effect and have negative impact on human health [2–7].

VOCs can originate from any natural sources such as volcanoes eruptions, biological processes, forest fires and geological beds [8]. However, human activities (e.g. transport, chemical and petrochemical industry, waste utilization plants, use of organic solvents) considerably increase the level of VOCs' emission [9–11]. Many different methods of the VOCs' abatement are known, for example, cryogenic condensation [12–14], biofiltration [15], wet absorption methods [16] as well as catalytic oxidation [17,18] and thermal oxidation connected with recuperation [19]. Nevertheless, adsorption seems to be the most effective, cheapest and environmentally friendly technique of VOCs elimination. There is a large number of various solid adsorbents based on porous materials, e.g. zeolites [20], clays [21,22], MCM-48 [23], silicated MCM-41 and spherical ordered silicas [24,25], organomodified silica materials or organic–inorganic composites [26,27] and many different activated carbon species [28,29]. Activated carbons can be produced from carbon containing raw materials like biomass, waste polymer [30,31] and high-processed coal (hard and brown coal, charcoal). The carbon-based materials have been applied among other to capturing of coal mine methane [32], removal of organic solvents [33] as well as remediation of waste water. Typical activated carbons are characterized by ultramicroporosity, which causes diffusion limitations. For this reason, adsorption of high molecular adsorbate takes place only on the external surface of carbon particles resulting in an ineffectiveness of inner surface.

The accessible surface of active carbon can be extended by its deposition on a high surface, mesoporous support. Polymers (e.g. polyacrylonitrile) are the best carbon precursors in such a case. Polymer layers can be relatively easily deposited on a support surface and subsequently transformed into carbon by thermal

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treatment. However, the deposition method strongly determines the properties of carbon/support composites. The coating of various materials (e.g. silica, alumina, titania, zirconia, carbon nanotubes) with polyacrylonitrile (PAN) by impregnation with a polymer solution (*N*,*N*-dimethylformamide is mainly used as a solvent) have been reported [34]. The adsorption of acrylonitrile vapour on support surface or filling a support pore system with a liquid monomer followed by polymerization have been studied as well [35,36]. Moreover, electrospinning [37], dry-jet spinning [38,39] and photochemical [40] processes have been used for the PAN deposition.

In this work we propose a direct one-pot synthesis of polyacrylonitrile/silica combined materials by precipitation polymerization of acrylonitrile in an aqueous slurry of a support. The obtained materials were subsequently carbonized in a non-oxidative atmosphere, characterized (TG, low-temperature N_2 sorption, SEM and FTIR-DRIFT) and tested in adsorption of methyl–ethyl ketone (MEK) from gas phase. MEK was selected as the molecule representing a wide family of oxygen-containing derivatives of hydrocarbons, which are common indoor air pollutants.

2. Materials and methods

2.1. Sample preparation

Commercial silica gel (Polish Chemical Reagents) and two mesoporous silicas (SBA-15 and MCM-41) with particle size <120 μm were used as starting materials for polymer deposition.

The MCM-41 material was synthesized with a molar gel composition 1.00 tetraethylortosilicate (TEOS): 0.20 dodecyltrimethylammonium chloride (C_{12}TMACl): 3.01 NH_3: 0.70 isopropanol: 150.87 H_2O. A volume of 548 cm^3 of distilled water, 22.7 cm^3 of C_{12}TMACl (50% isopropanol/water 40/10 solution, Aldrich) and 44.0 cm^3 of ammonia solution (25%, Polish Chemicals Reagents) were mixed in a 1 dm^3 beaker and stirred for 30 min at room temperature. Then, 48.6 cm^3 of TEOS (98%, Aldrich) was added. The resulting suspension was stirred for next 1 h. Subsequently, the product was filtered, washed with distilled water and dried at 313 K.

Mesoporous silica SBA-15 was synthesized according to the procedure described earlier [41] using a molar gel composition 1.00 TEOS: 0.02 Pluronic 123: 5.58 HCl: 182.55 H_2O. An 4.0 g amount of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer ($EO_{20}PO_{70}EO_{20}$, Pluronic P123) was dissolved in 150 cm^3 of 1.6 M HCl solution and then 9.14 cm^3 of TEOS was added. The obtained suspension was stirred at 318 K for 8 h and subsequently aged at 353 K for 15 h. The solid product was filtered, washed with distilled water and dried at room temperature.

To remove the template the dried SBA-15 and MCM-41 sieves were calcined at 823 K for 8 h at a heating rate of 1 K/min.

The organic-silica composite materials with the various intended PAN/support mass ratios (0.1, 0.2, 0.4, 0.6, 0.8, 1.2, 1.6 and 2.0) were synthesized by radical polymerization of acrylonitrile (AN) in the aqueous slurry of a silica support. 3 g of the support was introduced into a three-neck flask (250 cm^3) equipped with a reflux condenser. Then, adequate volumes of water, acrylonitrile (AN) and initiator solution (0.3 g of 2,2′-azobis(isobutyronitrile) hydrochloride, AIBA, dissolved in 25 cm^3 of water) were added to achieve the total mixture volume of 100 cm^3. The AIBA/AN molar ratio was kept at a constant level of 0.004, whereas the intended PAN/support mass ratios were obtained by the use of appropriate AN volume. During the whole polymerization process, the mixture was purged with argon at a flow rate of 40 cm^3/min. The process was performed at a temperature of 333 K for 3 h. The resulting composite material was filtered and washed with distilled water. The amount of the unreacted monomer in the filtrate was determined by the titration technique. Sodium hydroxide formed in the following reaction:

$$H_2C = CH - CN + Na_2SO_3 + H_2O \rightarrow NaSO_3 - CH_2 - CH_2 - CN + NaOH$$

was titrated with a 0.1 M HCl solution using phenolphthalein as an indicator.

The same procedure was applied to the synthesis of unsupported PAN which was a reference sample. In this case, the reaction mixture contained 3.72 cm^3 of AN, 91.17 cm^3 of distilled water and 5.11 cm^3 of AIBA solution.

The obtained PAN/support precursors were dried at 333 K overnight. Subsequently, the samples were carbonized in a tubular oven at a temperature of 623 K for 4 h, a heating rate was 5 K/min. The conditions of PAN/silica composites' carbonization were selected as optimal basing on our previous study [42]. The inert gas (argon; grade 4.6) flowed continuously by the oven at a flow rate of 40 cm^3/min during the whole thermal treatment process and cooling down to room temperature.

2.2. Characterization

Both the dried and carbonized PAN/support samples were analyzed by thermogravimetric method (TG-SDTA) using a Mettler Toledo TGA/SDTA 851 instrument. Argon or air flowed (80 cm^3/min) by a sample (approximately 25 mg), which was heated in a platinum crucible from 303 to 1273 K at a heating rate of 10 K/min.

The textural parameters of the thermally treated materials were determined by means of low-temperature adsorption of nitrogen (77 K). The adsorption–desorption isotherms were collected in an ASAP 2010 instrument (Micromeritics). Before the analysis, the samples were outgassed at 473 K for 12 h. The collected data were analyzed using the BET (surface area, S_{BET}) and *t*-plot (micropore volume, V_{micro}) models. Total pore volume (V_{total}) was calculated by single point method at the relative pressure of 0.97–0.98. The BJH procedure was used for calculating mesopore volume (V_{meso}), pore size distribution and mean mesopores diameters following the adsorption branch of the isotherm.

The morphology and surface composition of the samples were investigated using a HITACHI S-4700 field emission scanning electron microscope (FESEM) equipped with a NORAN Vantage energy dispersive spectrometer (EDS).

The composite structure was investigated using diffuse reflectance infrared Fourier transform spectroscopy (FTIR-DRIFT). Prior to analyses, the samples were diluted to 2% by weight in KBr. The spectra were recorded on Thermo Scientific Nicolet 6700 FT-IR spectrometer. 200 scans were collected each at a resolution of 4 cm^{-1}.

2.3. Adsorption tests

2.3.1. Dynamic adsorption

An amount of ca. 100 mg of a thermally treated sample was weighed in a small glass vessel. The open vessel was kept in a dryer at 423 K for 0.5 h (a preliminary outgassing step). After evacuation, the vessel was weighed again in order to determine strictly the mass of the dried sample. Then, the adsorbent was quantitatively transferred into a stainless steel reactor with a total volume of 1.2 cm^3. The constant flow of the carrier gas (N_2, 20 cm^3/min), saturated with methyl–ethyl ketone (MEK) vapour at saturation temperature of 283 K, was passed by an adsorber placed in an oven (313 K). The outlet of the adsorber was directly connected to a flame ionization detector (FID). The sorption capacity of a sample was detected by the intensity of the FID signal attaining a constant