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Synthesis of carbon/α-Al$_2$O$_3$ composite adsorbents for the elimination of methyl ethyl ketone vapour[**)]

Summary — α-Al$_2$O$_3$ has been modified by the deposition of different amounts of polyacrylonitrile (PAN) *via* precipitation radical polymerization in an aqueous suspension. Carbonization of the product performed in an inert atmosphere at 350 °C resulted in obtaining of a carbon layer supported on the surface of α-Al$_2$O$_3$. The content of carbon in the composites was determined by temperature-programmed oxidation, whereas textural properties of the synthesized samples were studied by low-temperature sorption of N$_2$ (BET). The carbon/α-Al$_2$O$_3$ composites appeared to be effective adsorbents of methyl ethyl ketone vapour.

Key words: polyacrylonitrile, aluminum oxide (α-Al$_2$O$_3$), composite materials, deposition, carbonization, adsorbents, volatile organic compounds.

OTRZYMYWANIE KOMPOZYTOWYCH ADSORBENTÓW WĘGIEL/α-Al$_2$O$_3$ DO ELIMINOWANIA PAR KETONU METYLOWO-ETYLOWEGO

Streszczenie — Zmodyfikowano powierzchniowo tlenek glinu osadzając na nim w wyniku prowadzonej w wodnej zawiesinie α-Al$_2$O$_3$ rodnikowej polimeryzacji akrylonitrylu różne ilości PAN (2,3; 3,1 lub 3,8 moli PAN na 1 mol tlenku glinu). Badania termograwimetryczne wykonane w przepływie gazu obojętnego (rys. 1) pozwoliły na określenie mechanizmu termicznego rozkładu tak osadzonego PAN oraz na wytypowanie optymalnej temperatury karbonizacji uzyskanych materiałów prekursorowych (350 °C w argonie). Wyniki temperaturowo-programowanego utlenienia (rys. 2) umożliwiły zdefiniowanie stabilności termicznej karbonizatów w atmosferze powietrza oraz wyznaczenie zawartości w nich węgla; wyniosła ona (w zależności od udziału PAN) 12,8; 25,8 lub 42,1 % mas. C. Zaobserwowano, że zawartość ta jest skorelowana z parametrami teksturalnymi (powierzchnią właściwą oraz całkowitą objętością porów) karbonizowanego materiału (tabela 1). Powierzchnia właściwa wyznaczona metodą BET maleje z 29,1 m^2/g (niemodyfikowany α-Al$_2$O$_3$) do 13,1 m^2/g w przypadku próbki z największą zawartością C. Preparaty przetestowano w roli adsorbentów par ketonu metylowo-etylowego (MEK) z powietrza (rys. 3). Stwierdzono wyraźny wzrost efektywności adsorpcji spowodowany obecnością węgla, zwiększającej się wraz ze zwiększaniem zawartości C, do 0,0201 g MEK na 1 g adsorbenta.

Słowa kluczowe: poliakrylonitryl, tlenek glinu (α-Al$_2$O$_3$), materiały kompozytowe, osadzanie warstw polimerowych na nośniku, karbonizacja, adsorbenty, lotne związki organiczne.

Volatile organic compounds (VOCs), which are discharged into the atmosphere by various industrial processes, have been classified as dangerous chemical pollutants. The acceptable level of VOCs concentration in the air has been regulated by European Community Directive 2001/81 and U.S. Clean Air Act Amendments [1]. The emission of VOCs can be limited by different methods such as condensation, adsorption, catalytic oxidation and thermal oxidation [2, 3]. Among them, adsorption being a highly effective and low cost process is commonly considered to be the best way of the VOCs abatement. Typically, active carbon-based adsorbents prepared from a wide range of high carbonaceous content materials are used in VOCs adsorption [4—12]. Nevertheless, this type of product is characterized by ultramicroporosity which limits accessibility of organic molecules to the inner sur-

face. Thus, in the adsorption process only the sites located on the external surface of the carbon particles are active.

In the presented work, we have demonstrated a new approach for the extension of the carbon surface by the deposition of a carbon layer on an inorganic support. Different amounts of carbon were introduced by precipitation polymerization of acrylonitrile in an aqueous suspension of the support followed by thermal treatment in an inert atmosphere. We have tested the prepared materials as adsorbents for methyl ethyl ketone vapour.

EXPERIMENTAL

Composites preparation

Polyacrylonitrile (PAN) was deposited on the surface of α-Al_2O_3 (produced by POCh, Gliwice) by radical precipitation polymerization of acrylonitrile (AN, produced by Aldrich) performed in an aqueous suspension of the this inorganic support. To this purpose freshly distilled AN was dissolved at 25 °C in water containing Al_2O_3 using three different $AN:Al_2O_3$ molar ratios, namely 2.3 ($PAN2,3/Al_2O_3$), 3.1 ($PAN3,1/Al_2O_3$) and 3.8 ($PAN3,8/Al_2O_3$). The resulting suspensions were purged with argon for 30 min, subsequently the initiator — 2,2'-azo-bis(isobutyramidine dihydrochloride (AIBA, Aldrich) — was added at an AIBA:AN molar ratio of 0.004 and the whole system was heated to 60 °C. The solid material from each suspension was isolated after 3 h of heating by filtration, washed with distilled water and dried under vacuum at 50 °C. Finally, the synthesized composite was calcined in a flow of argon (80 ml/min) at 350 °C at a heating rate of 5 °C/min and an isothermal period of 4 h.

Methods of testing

Thermal analysis (TG/DTG/SDTA) (SDTA = Simultaneous Differential Thermal Analysis) was performed using a Mettler Toledo TGA/SDTA 851^e instrument equipped with a Thermo Star (Balzers) quadrupole mass spectrometer. A constant flow of argon or air (80 ml/min) was passed through the sample (approximately 10 mg), which was heated in a corundum crucible from 30 to 1000 °C at a heating rate of 10 °C/min.

The textural parameters of the carbonized materials were determined using adsorption of nitrogen at -196 °C (BET).

The adsorption-desorption isotherms were collected in an ASAP 2010 instrument (Micromeritics). The calcined sample (0.2 g) was contacted with static vapour present over 5 ml of methyl ethyl ketone (MEK, produced by Chempur, Piekary Śląskie) in 200 ml vessel. The closed reaction vessel was kept in a dryer at 40 °C for 48 h. After adsorption, the vessel was opened and the used adsorbent exposed to atmospheric air at 30 °C for 10 min. Then, the solid was weighed, transferred to a quartz tubular

reactor with the outlet connected directly to a flame ionization detector (FID). The desorption was performed by heating the sample from 50 to 650 °C at a heating rate of 15 °C/min in a stream of pure nitrogen (10 ml/min). The recorded FID signal was used to determine the amount of MEK adsorbed.

RESULTS AND DISCUSSION

As it was stated before the as-synthesized PAN/Al_2O_3 composites were studied by the TG and SDTA methods in a stream of inert gas in order to optimize the conditions of subsequent oxygen-free carbonization. An example of the obtained results for the $PAN3,1/Al_2O_3$ sample is presented in Fig. 1. It was observed that the deposited polymer is stable on the surface of α-Al_2O_3 up to about 290 °C — a loss of sample mass attributed to PAN decomposition was detected above this temperature. At 310—320 °C intensive peaks in the DTG and SDTA curves were distinguished. It should be noted that the first stage of polymer
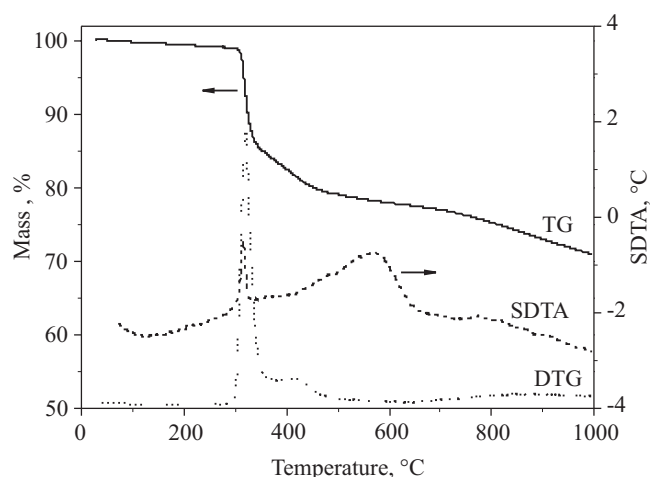

Fig. 1. Thermal analysis (TG-SDTA) of the PAN3,1/Al$_2$O$_3$ composite performed in a stream of inert gas

degradation, which is usually assigned to exothermic cyclization of PAN chains [13,14], occurs in a very narrow temperature range suggesting a homogeneous distribution of deposited PAN.

To avoid deep condensation resulting in graphitization of the carbon layer, an optimal temperature of 350 °C for the thermal treatment of the composite materials prior to adsorption tests was chosen. The carbonized samples were examined by temperature-programmed oxidation (Fig. 2). An interesting effect of an increase in the sample mass is observed in a temperature range of 160—260 °C. It could be assumed that the carbonized material was mildly oxidized to form oxygen-containing surface species in this stage. A further rise in temperature caused a drop in the sample mass which can be attributed to a progressive carbonisation of PAN (endothermic process
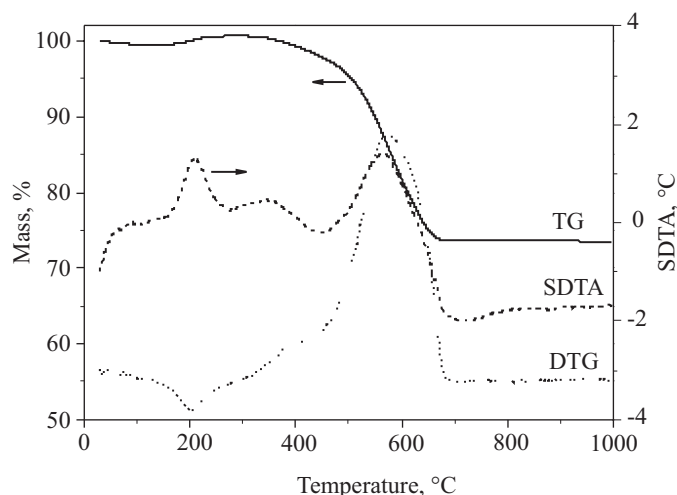
Fig. 2. Temperature-programmed oxidation of the PAN3,1/Al₂O₃ sample activated thermally at 350 °C in oxygen-free atmosphere

above 330 °C) and subsequent burning of carbon layer deposited on the α-Al₂O₃ surface (exothermic process above 450 °C).

These results of the temperature-programmed oxidation were used to determine the carbon content in the synthesized samples (Table 1).

T a b l e 1. Properties of the samples calcined at 350 °C for 4 h

Sample	Carbon content wt. %	BET surface area m²/g	Total pore volume cm³/g	Effectiveness of MEK adsorption g_{MEK}/g_{ads}
α-Al₂O₃	—	29.1	0.060	0.0001
PAN2,3/Al₂O₃	12.8	22.7	0.047	0.0039
PAN3,1/Al₂O₃	25.8	16.0	0.028	0.0127
PAN3,8/Al₂O₃	42.1	13.1	0.020	0.0201

An increase in carbon loading from 12.8 to 42.1 wt. % was observed with an increase in AN:Al₂O₃ molar ratio from 2.3 to 3.8 during the initial stage of the composite synthesis. Obviously, a higher concentration of the monomer in an aqueous suspension favours a more effective deposition of PAN on the α-Al₂O₃ surface.

Furthermore, an introduction of carbonaceous material results in a change of textural properties of the α-Al₂O₃-supported samples. BET surface area and total pore volume decrease with an increase in carbon loading (Table 1). For the PAN3,8/Al₂O₃ composite, a drop of 55 % of surface area and 67 % of total pore volume was observed in a relation to the non-modified α-Al₂O₃ support. Evidently, a deposited polymer partially blocks the pore system existing inside and between α-alumina particles. However, interparticle porosity of the support is maintained even at the highest carbon content.

The carbon/α-Al₂O₃ composites were prepared to be tested as adsorbents of volatile organic compounds. For preliminary studies, methyl ethyl ketone vapour was selected as the adsorbate. This molecule represents both hydrophobic hydrocarbon compounds and hydrophilic oxygenates. As it was described above, the adsorption process was performed at 40 °C, and the samples were conditioned in static air prior to the desorption experiment. Such experimental procedure should clearly show which kind of material can be considered useful as adsorbent for odour control.

The desorption profiles recorded for the samples after 48 h exposure to MEK vapour are comparatively illustrated in Fig. 3. It should be noted that MEK molecules are adsorbed very poorly on unmodified α-Al₂O₃. In this case, the adsorption effect can be assigned to surface acid/base interaction. The octahedral Lewis acid sites present solely on the α-Al₂O₃ surface are significantly weaker than the tetrahedral ones which can be found on the surface of γ-Al₂O₃ [15]. This latter kind of alumina is often tested as ketones and aldehydes adsorbent capable to transform these molecules into the corresponding products [16—18].
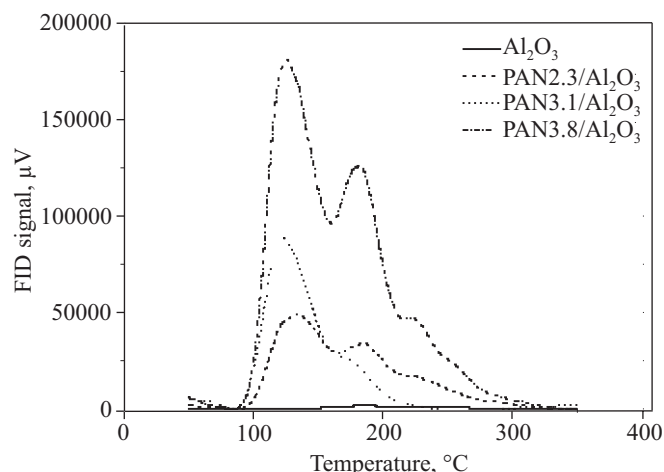

Fig. 3. Temperature-programmed desorption of MEK for the carbon/Al₂O₃ composites after contact with MEK vapour at 40 °C for 48 h

The modification of the support with carbonaceous material results in a significant increase of an amount of MEK desorbed from a sample. Different types of adsorption sites varying in adsorption strength can be distinguished on the formed carbon layer. This effect is manifested by at least three peaks present in the temperature-programmed desorption profiles. The measured FID signal allows for the calculation of the total concentration of surface sites active in the MEK adsorption. The determined values of the adsorption effectiveness, defined as the amount of MEK in grams adsorbed per 1 g of an adsorbent, are shown in the last column of Table 1. It

can be found that the adsorption effectiveness strongly depends on carbon loading, namely the sample PAN3,8/Al$_2$O$_3$ containing the highest amount of carbon exhibits the highest performance in MEK adsorption.

CONCLUSIONS

A new method of the modification of inorganic supports (such as α-Al$_2$O$_3$ presented in this paper) with a carbon material has been proposed. Polyacrylonitrile deposited by the precipitation polymerization in an aqueous suspension of α-alumina is an attractive precursor of carbon layer. The transformation of polymer into the corresponding carbonizate can be achieved by an oxygen-free calcination. The carbon content in the obtained composites can be adjusted by a change of the monomer:support molar ratio during the synthesis. As the result, effective adsorbents for a removal of methyl ethyl ketone vapour are obtained.

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