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USE OF ACENAPHTHENE AS A CARBON PYROLYZATE CARRIER FOR THE PREPARATION OF ALUMINIUM-CARBON SORBENTS

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The purpose of this study was a preliminary evaluation of mineral-carbon sorbents preparation possibility by the method of thermal decomposition of a mixture of aluminium oxide or hydroxide and acenaphthene and determination of their physicochemical properties. The conditions of carbonization were established and the changes of physicochemical properties of obtained materials as a function of organic substance content in the mineral-carbon mixture before the process of carbonization were tracked. In these investigations the methods of thermal analysis, low-temperature nitrogen adsorption and benzene vapors adsorption were applied.

Keywords: *acenaphthene, aluminium hydroxide, mineral-carbon sorbents*

Introduction

Mineral-carbon sorbents belong to a group of new materials consisting of two components: mineral ingredient, constituting a mineral matrix and organic component. These sorbents are prepared by mechanical mixing of two components, i.e. mineral substance and carbon substance as well as by embedding carbon substance into the structure of the mineral or incorporating particles of carbon adsorbent amidst the particles of a gel [1–3].

In the literature, there are known possibilities of use of acenaphthene for the preparation of complex sorbents, especially when silica is used as a mineral matrix. It was demonstrated that acenaphthene easily undergoes the processes of pyrolysis leading to the formation of condensed carbon structures, distinctive for active carbon [4]. In connection with these reports, it seems purposeful to conduct studies on the evaluation of possibilities of application of aluminium hydroxides and oxides, having high specific surface, and acenaphthene as a carrier of carbon pyrolyzate for the preparation of aluminium-carbon sorbents. Sorbents of this type could find applications inter alia in the purification of hydrocarbon polluted wastewaters [5–7].

Experimental

Acenaphthene was used as a carbon pyrolyzate carrier and two initial mineral matrices were applied: aluminium hydroxide and aluminium hydroxide after 30 min of calcination in the temperature of 500°C, leading to the formation of hydrated aluminium oxide.

Pure acenaphthene produced by POCh, Gliwice, Poland and samples of aluminium hydroxide prepared under established conditions, having high porosity, were utilized in the study. Aluminium chloride (analytically pure, produced by POCh Gliwice) was used as a precursor for aluminium hydroxide precipitation, which was conducted by means of ammonia solution. Precipitated hydroxide was kept in the initial solution for five hours.

A series of compositions having different proportions of organic component and mineral matrix, containing 9 to 33 mass% of acenaphthene in the initial mixture with aluminium hydroxide or oxide before carbonization.

Weighed amounts of aluminium hydroxide or oxide and acenaphthene were ground thoroughly in a mortar in order to homogenize the mixture. Afterwards, the samples were carbonized in 500°C for 30 min under nitrogen atmosphere.

In order to evaluate the structural properties of mineral matrix samples and mineral-carbon samples, adsorption studies in a glass vacuum apparatus were carried out: volumetric measurements of low temperature adsorption of nitrogen and measurements of benzene vapors adsorption by McBain–Bakr gravimetric method. ‘Izotermy’ computer software [8] was utilized in order to calculate the specific surface. The calculations were based on BET method.

Thermal analysis studies were carried out by means of computer controlled TA Instruments SDT 2960 thermobalance. Samples, weighing about 10 mg were heated in air with the temperature increase ratio of 10°C min^{-1}, in the range of temperatures from 20 to 1000°C.

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Results and discussion

Thermal analysis was conducted for samples of initial mineral matrices (aluminium hydroxide and oxide) and mineral-carbon sorbents obtained in 500°C, 30 min time and under nitrogen atmosphere. Exemplary TG curves are presented in Figs 1 and 2.

During thermal analysis of aluminium hydroxide, three endothermic effects were observed on the TG curve. The first one has an extremum at 80°C, related to the release of physically adsorbed water. At 250°C dehydration of gibbsite (aluminium hydroxide) occurs and the extremum at 460°C is related to the dehydration of boehmite (aluminium metahydroxide) [9–11].

The results of thermal analysis of calcination products of aluminium hydroxide with different initial content of acenaphthene (from 9 to 33 mass%) indicate that, in the qualitative respect, the course of thermal decomposition is similar (Fig. 1). As a result of previous calcination of samples in the 500°C/30 min/nitrogen conditions, dehydration of hydroxide to oxide occurred as well as pyrolysis of organic substance. The process of decomposition occurs in two stages. The first stage is a release of physically adsorbed water, taking place in the range of temperatures from 20 to 150°C. For all studied samples the values of mass losses are comparable and amount to about 7 mass%. In the second stage, in the range of temperatures from 150 to 1000°C, combustion and thermal decomposition occur of organic substance (carbon pyrolyzate), deposited on a mineral matrix during carbonization. In this stage also the occurrence of aluminium hydroxide dehydration is not ruled out, which could be inhibited during carbonization by deposited layer of carbon pyrolyzate.

Superimposing effects of carbon pyrolyzate combustion and dehydroxylation of mineral matrix in the second stage of thermal decomposition significantly renders the evaluation of carbon residues content in carbonizates difficult. Particularly in the case of discussed samples higher mass losses on a TG curve (Fig. 1) can be observed compared to the pure aluminium oxide. Total mass loss of carbonizates in 1000°C varies from 15 to 16.5 mass%, while for aluminium oxide it is 11.5%. The content of carbon pyrolyzate is not significant and can reach up to 5 mass%. It should be noticed that the amount of carbon pyrolyzate in the samples increases disproportionately related to the amount of introduced organic component. For example, samples containing 29 and 33% of initially introduced organic substance exhibit comparable mass loss during thermal analysis, amounting to 16.5 mass%.

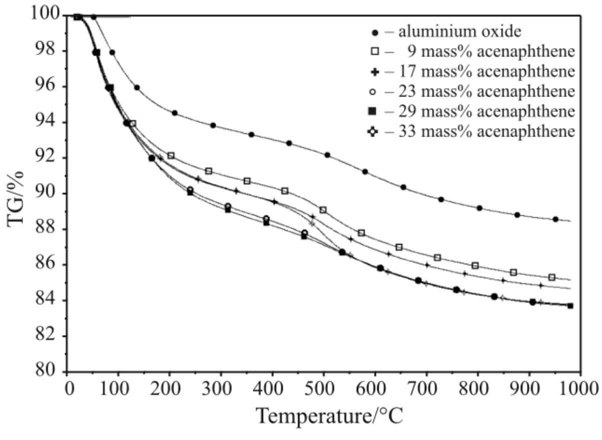

Fig. 1 TG curves for carbonizates obtained from aluminium hydroxide and acenaphthene in 500°C, during 30 min, under nitrogen atmosphere

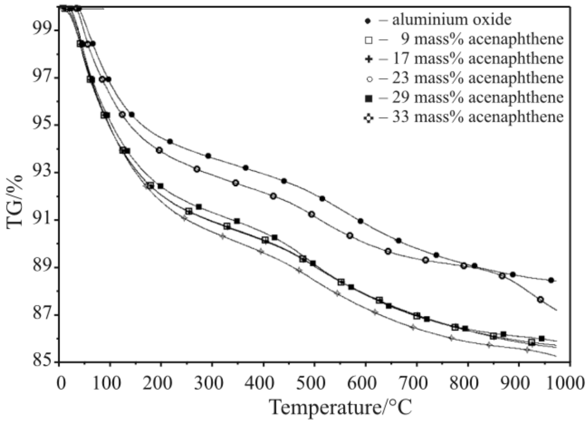

Fig. 2 TG curves for carbonizates obtained from aluminium oxide and acenaphthene in 500°C, during 30 min, under nitrogen atmosphere

Comparing the TG curves for the initial organic matrix (aluminium oxide) and carbonizates based on this matrix (Fig. 2) it can be concluded that the content of carbon pyrolyzate varies from 1.5 to 2.5 mass% while total mass loss of carbonizates during thermal analysis up to 1000°C ranges from 13 to 14 mass% and does not change proportionally with the increase of initially introduced organic substance content.

Table 1 presents the results of specific surface measurements, conducted on the basis of low-temperature nitrogen adsorption and benzene vapor adsorption.

Analyzing data obtained on the basis of low-temperature nitrogen adsorption (Table 1), it was found that the sample of initial aluminium hydroxide has the lowest specific surface S_{BET}. Increase of acenaphthene content in the mixture with aluminium hydroxide from 9 to 23 mass% results in the increase of samples porosity after carbonization. It is caused by both dehydration of aluminium hydroxide and pyrolysis of organic substance occurring during thermal treatment. Higher amounts of acenaphthene (samples containing 29 and 33 mass% acenaphthene) cause the decrease of S_{BET} specific surface. For the above men-

Table 1 Specific surface values for mineral-carbon sorbents obtained in the 500°C/nitrogen/30 min conditions, determined by the methods of nitrogen low-temperature adsorption and benzene vapor adsorption

Composition of the mixture before carbonization (acenaphthene content)	S_{BET} specific surface/m^2 g^{-1} (nitrogen)	S_{BET} specific surface/m^2 g^{-1} (benzene)	
		horizontal	vertical
Aluminium hydroxide	173	195	121
Aluminium hydroxide+ 9 mass% acenaphthene	179	195	122
Aluminium hydroxide+ 17 mass% acenaphthene	203	–	–
Aluminium hydroxide+ 23 mass% acenaphthene	206	196	122
Aluminium hydroxide+ 29 mass% acenaphthene	194	–	–
Aluminium hydroxide+ 33 mass% acenaphthene	197	157	98
Aluminium oxide	213	235	147
Aluminium oxide+ 9 mass% acenaphthene	201	206	128
Aluminium oxide+ 17 mass% acenaphthene	194	–	–
Aluminium oxide+ 23 mass% acenaphthene	198	236	147
Aluminium oxide+ 29 mass% acenaphthene	197	–	–
Aluminium oxide+ 33 mass% acenaphthene	191	210	131

tioned samples, the contribution of carbon pyrolyzate to the formation of porous structure increases. Furthermore, higher amounts of carbon pyrolyzates deposited on the inorganic matrix can cause inhibition of aluminium hydroxide dehydration, which leads to the decrease of porosity of obtained sorbents.

Aluminium oxide obtained after calcination of hydroxide in the 500°C/nitrogen/30 min conditions has higher specific surface than the initial substance. The processes of dehydration and dehydroxylation of surfaces occurring during isothermal treatment cause the development of porous structure.

For the samples of aluminium oxide with the initial content of acenaphthene ranging from 9 to 33 mass%, S_{BET} specific surface decreases with increasing amount of organic substance. It is caused by increasing amount of carbon pyrolyzate, which takes over the structure-building role.

Aluminium oxide during carbonization undergoes transformations to a smaller extent, so the decrease of specific surface of the samples can only be caused by the deposition of the carbon pyrolyzate layer in the pores.

The values of S_{BET} specific surface calculated assuming horizontal and vertical orientation of benzene molecules in the monomolecular layer were compared to the values obtained for low temperature adsorption of nitrogen.

It is well known that the chemical structure greatly influences sorption capacity of adsorbents because functional groups existing on the surface determine its hydrophilic-hydrophobic properties. In the case of aluminium hydroxide and oxide, hydrophilic properties are determined by hydroxyl groups present on the surface, preventing the horizontal orientation of benzene molecules.

In the case when the value of specific surface assuming horizontal orientation of benzene molecule in the monolayer is lower or equaling the S_{BET} surface calculated on the basis of nitrogen adsorption, one can conclude that the surface is hydrophobic and benzene molecules are oriented horizontally. When S_{BET} (horizontal) calculated for benzene adsorption is higher than specific surface based on nitrogen adsorption it means that the orientation of benzene molecules is mixed (skewed), characteristic for the hydrophilic surfaces [12–14].

From the comparison of S_{BET} values calculated on the basis of benzene vapors adsorption assuming horizontal and vertical orientations of benzene molecules and S_{BET} determined from the low-temperature nitrogen adsorption it can be concluded that the sample of initial aluminium hydroxide contains high amounts of surface hydrophilic centers preventing horizontal orientation of benzene molecules in the adsorption layer. The sample containing 9% of initially introduced acenaphthene has the surface non-uniformly covered with carbon pyrolyzate, which is testified by increased value of S_{BET} (horizontal), compared to S_{BET} calculated from nitrogen adsorption. It can be caused by too small amount of initially introduced organic substance. For the samples containing 23 and 33 mass% of acenaphthene the S_{BET} value is lower compared to the values obtained by nitrogen adsorption which can indicate that these samples are characterized by uniform coverage of surface with hydrophobic carbon pyrolyzate.

All samples with aluminium oxide as a mineral matrix have higher S_{BET} (horizontal) values compared to specific surface calculated from nitrogen adsorption. It can indicate non-uniform coverage of matrix surface with carbon pyrolyzate and skewed orientation of adsorbate molecules in an adsorption layer.

Benzene vapors adsorption and desorption isotherms for sorbents obtained by initial mixing of mineral matrix with 9, 23 and 33 mass% acenaphthene are presented in Figs 3 and 4.

Wide hysteresis loops for benzene vapors adsorption and desorption isotherms (Figs 3 and 4) indicate that the porous structure on the surface of samples is well developed, including pores of irregular shapes. The shape of isotherms for all studied samples, initial mineral matrices and sorbents alike, is similar, which indicates that the deposition of carbon pyrolyzate on the surface of mineral substance does not change significantly the structure of pores in obtained materials.

Obtained isotherms can be classified, according to the IUPAC nomenclature, to the H2 type. It meets the case of pores graphically described as an ‘ink-well’ and spherical pores with open endings and significant internal contractions.

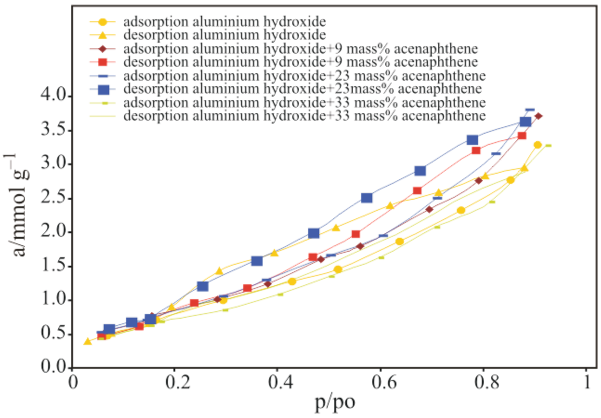

Fig. 3 Benzene vapours adsorption and desorption isotherms determined for sorbents with aluminium hydroxide as a mineral matrix, carbonized in 500°C, 30 min, under nitrogen atmosphere

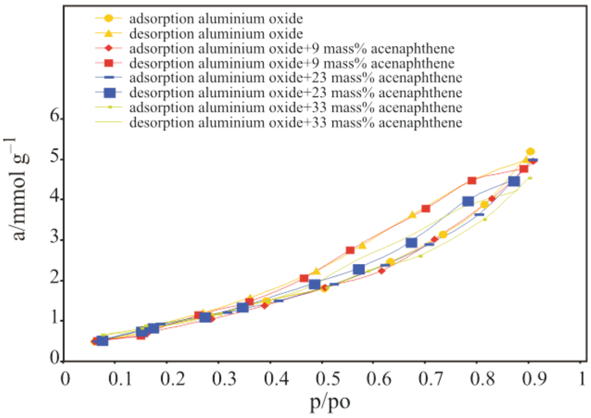

Fig. 4 Benzene vapours adsorption and desorption isotherms determined for sorbents with aluminium oxide as a mineral matrix, carbonized in 500°C, 30 min, under nitrogen atmosphere

The results of this study allow to ascertain that applied calculation models lead to a concordant picture of changes of the porous structure of carbonizates obtained from aluminium oxide and hydroxide modified with an organic substance. No micro-pores were found in the samples. All changes of porosity are related to the reduction or increase of surface of mesopores.

Distribution curves of surface of pores in relation to their effective radii, presented in Figs 5 and 6 were calculated assuming the model of cylindrical pores, open at both ends.

For the sample of initial aluminium hydroxide, there is a dominance of pores of 15 Å radii, and it exhibits a monodispersive distribution of pore surface (Fig. 5). The modification of aluminium hydroxide surface with acenaphthene causes significant changes in the structure of samples. For the samples containing 9, 23 and 33 mass% initially introduced ace-

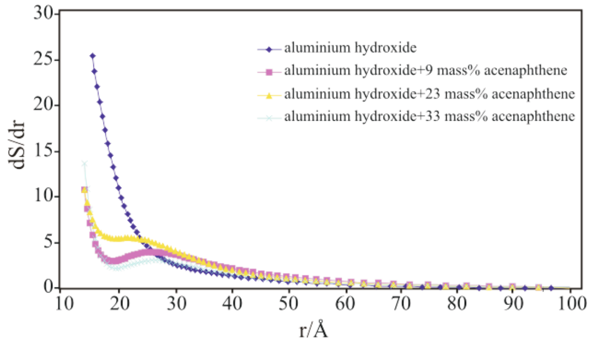

Fig. 5 Pore surface distribution curves related to effective radii for the sample of aluminium hydroxide and sorbents obtained from aluminium hydroxide with 9, 23 and 33 mass% acenaphthene, carbonized in 500°C for 30 min under nitrogen atmosphere

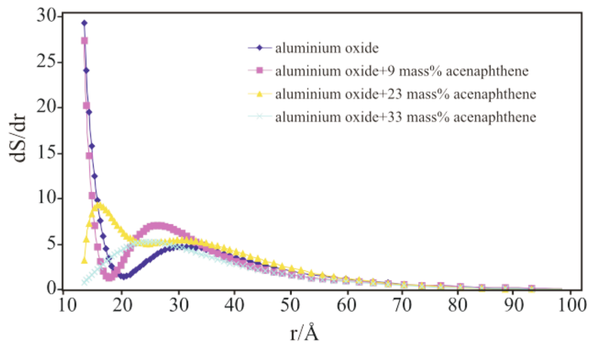

Fig. 6 Pore surface distribution curves related to effective radii for the sample of aluminium oxide and sorbents obtained from aluminium oxide with 9, 23 and 33 mass% acenaphthene, carbonized in 500°C for 30 min under nitrogen atmosphere

naphthene, d*S*/d*r* curves have bimoidal features. There are two maxima in the range of 15 and 30 Å.

The appearance of an additional maximum is related to the formation of a new porous structure of a deposited carbon pyrolyzate.

In the case of samples obtained on the basis of aluminium oxide as a mineral matrix, a bimodal distribution of pore surface is observed for both the initial matrix and mineral-carbon sorbents obtained after carbonization (Fig. 6). Pores of effective radii about 15 and 35 Å dominate in these samples. The only exception is the sample with 33 mass% acenaphthene in the initial mixture, which is monodispersive (there is a dominance of pores having effective radius of 30 Å).

Congenial character of pore surface distribution curves for samples with oxide as a mineral matrix, indicates that carbon pyrolyzate deposited on matrix surface does not significantly influence the change of porous structure.

Conclusions

- Basing on the results of conducted studies it was found that addition of 23 mass% acenaphthene to aluminium hydroxide is more efficient,
- Aluminium-carbon sorbent obtained after carbonization is characterized by a distinct mesoporous structure compared to the initial matrix, highest value of specific surface and hydrophobic properties,
- A material of this type can be used in the processes of hydrocarbon polluted wastewaters purification.

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