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ADSORPTION AND POROSITY PROPERTIES OF CARBON-COVERED ALUMINA SURFACES

M. Błachnio[1], *P. Staszczuk*[1*], *G. Grodzicka*[1], *L. Lin*[2] *and Y. X. Zhu*[2]

[1]Department of Physicochemistry of Solid Surface, Chemistry Faculty, Maria Curie-Skłodowska University
Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland
[2]State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, 100871 Beijing, China

Uniformly carbon-covered alumina (CCA) was prepared via the carbonisation of sucrose highly dispersed on the alumina surface. Using special thermogravimetry and sorptometry methods physicochemical properties of carbon-covered alumina surfaces were investigated. A numerical and analytical procedure for the evaluation of total heterogeneous properties (desorption energy distribution and pore-size distribution functions) on the basis of liquid thermodesorption from the sample surfaces under the quasi-equilibrium conditions are presented. The desorption energy distribution was derived from the mass loss Q-TG and the differential mass loss Q-DTG curves of thermodesorption of pre-adsorbed polar and apolar liquid films. For the first time, the evaluation of the fractal dimensions of carbon-covered alumina using the sorptometry, thermogravimetry and AFM data is presented.

Keywords: *carbon-covered alumina, fractal dimensions, sorptometry, thermogravimetry, total heterogeneity*

Introduction

Carbon and alumina probably are the most widely used support materials for catalyst systems. Nevertheless, both of them have drawbacks. Most carbon materials either are microporous or have poor mechanical properties. Therefore, in some reactions involving large molecules on carbon-supported metal catalysts, the metal particles are deposited in the carbon micropores, making their effects on the catalytic activity trivial. In addition, most mesoporous carbon materials are not favourable supports because of their poor crushing strength, low bulk density, or low surface area. Alumina, under certain conditions, also has its own disadvantages, such as its acidity and strong interaction with metals. To overcome these shortcomings, a new approach was developed in which the Al_2O_3 surface was coated with a thin layer of carbon prior to metal impregnation. In this way, the favourable carbon surface properties are combined with the optimal textural and mechanical features of the Al_2O_3 support. This synergetic effect makes carbon-covered alumina (CCA) superior to pure alumina and pure carbon in some cases.

Along with its use in catalysis, CCA also is a carbon-mineral adsorbent that represents a new type of adsorption materials containing two components: mineral and carbonaceous species. They have dual functions as a polar inorganic adsorbent and a nonpolar carbon adsorbent. This enables them to adsorb both organic and inorganic substances. The performance of such adsorbents in adsorption process depends on their physicochemical properties [1].

Experimental

Materials and methods

The materials for the investigations were obtained from State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University.

Typical procedure for the synthesis of CCA was as follows. First the sucrose/γ-Al_2O_3 precursors were prepared by impregnation of commercial γ-Al_2O_3 with aqueous solutions of sucrose. After being dried at 90°C, the precursors were calcined at 600°C in N_2 for 5 h. The final product was denoted as CCA03. To obtain uniformly CCA with higher carbon content, CCA03 was further impregnated with an aqueous solution of sucrose to give CCA03-2.

Thickness of the adsorbed liquid layers on the surface can be assessed by means of immersion mode of the solid samples. Adsorption of apolar (benzene and *n*-octane) and polar (water and *n*-butanol) liquid layers was measured using the derivatograph Q-1500 D (MOM, Hungary). The samples were saturated with liquid vapors in the vacuum desiccator at $p/p_0=1$. The Q-TG mass loss and Q-DTG differential mass loss

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* Author for correspondence: piotr@hermes.umcs.lublin.pl

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

curves were measured under the quasi-isothermal conditions in the temperature range 20–250°C at a heating rate of 6° min^{-1}.

Porosity properties e.g. specific surface areas, pore size distribution and pore volume were calculated from low-temperature nitrogen adsorption-desorption isotherms measured by means of the Sorptomat ASAP 2405 V1.01 (Micrometrics Co., USA). In order to characterize fully the structure of pure Al_2O_3 and CCA surface AFM pictures were also obtained by means of the Digital Instruments (USA) NanoScope III type and scanning microscopy EDX LEO SEM 1430VP type.

Results and discussion

Studies of the structure of pure and carbon covered alumina, which are presented, were used by means of independent research methods i.e. sorptometric measurements, liquid thermodesorption under quasi-static conditions, scanning and atomic force microscopy.

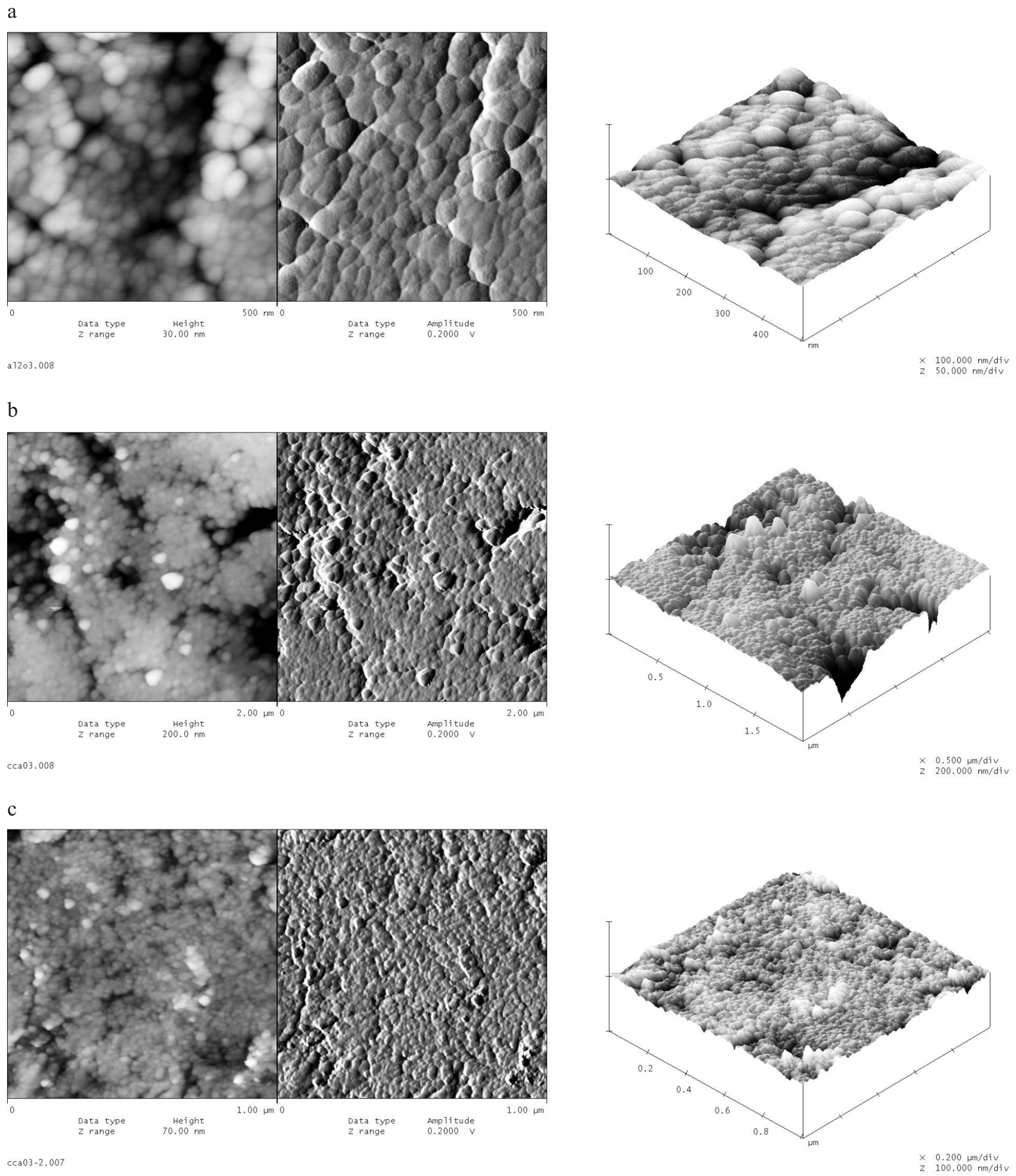

Fig. 1 AFM photos of a – Al_2O_3, b – CCA03 and c – CCA03-2 surface samples

Figures 1 and 2 present the exemplary photos made by means of AFM and SEM microscope.

The adsorption-desorption nitrogen isotherms at 77 K (Fig. 3) plotted from a large number of experimental points can be included in type IV according to the BET (Brunauer–Emmett–Teller) classification. This type of isotherms describes the process of nitrogen physical adsorption on the adsorbent surface. As pure and carbon covered alumina have a heterogeneous porous structure, the pores of the smallest diameters-micropores are filled up at small pressures of the adsorbate. With the increasing concentration of the adsorbate in the gaseous phase, pores of larger and larger diameters are filled up and the multimolecular adsorption layer is formed. The presence of the hysteresis loop in the diagrams gives evidence for occurrence of open pores in the studied adsorbents. The adsorption capacities read from the isotherms are characterized by moderate values. The samples of Al_2O_3 and CCA03 have similar adsorption capacities i.e. 340 and 330 cm^3 g^{-1}. For the sample of CCA03-2 value is 270 cm^3 g^{-1}.

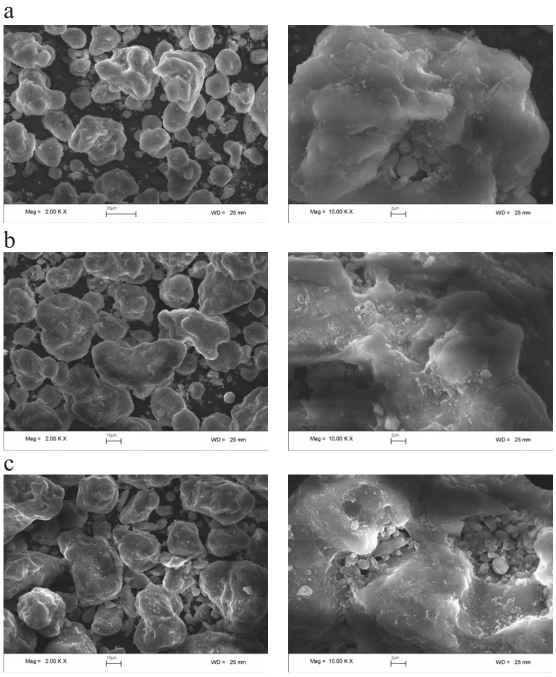

Fig. 2 SEM photos of a – Al_2O_3, b – CCA03 and c – CCA03-2 surface samples

Characteristics of microporosity could be made using the isotherms in the case when the values P/P_0 would include ultra-low values (below 0.01). As the relative pressure conditions of nitrogen vapour were insufficiently low of the order 0.06, the obtained isotherms were used only to determine mesoporosity. The parameters characterizing microporosity i.e. the specific surface area and micropores volume were determined using the method elaborated by Lippens and de Boera.

To obtain complete information about texture of the studied materials there were analysed the following parameter: specific surface area, pore volume, pore size (Table 1) and pore size distribution curves of alumina, CCA03 and CCA03-2 calculated from the desorption branches of the isotherms according to the BJH method (Fig. 4). The specific surface area of micropores for the CCA03 sample decreased slightly. The double loading process with carbon caused double increase in the specific surface area of micropores. The values of the specific surface area (S_{BET}) changed in the range 128–171 cm^3 g^{-1} for the samples and form the series Al_2O_3<CCA03<CCA03-2. These changes are due to creation new pore structures of investigated materials after the modification processes. The decrease of the mean value of pore diameter from 15 to 12 and 10 nm with the increasing specific surface area is observed. The analogous relationship in the case of the pore volume calculated from desorption data and specific surface area is observed.

The shape of pore size distribution curves of materials calculated from the desorption branches of the isotherms is similar to the Gauss curves with one distinct peak near value of 5 nm for Al_2O_3, CCA03-2 and 7 nm for CCA03 sample. The pores of these diameters have the largest contribution in sorption.

The thermodesorption method under the quasi-isothermal conditions used to study properties of the

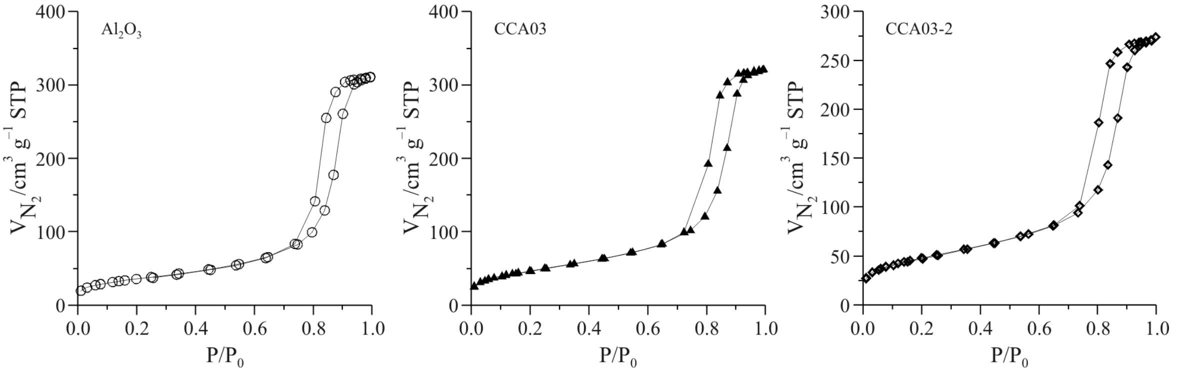

Fig. 3 Isotherms of nitrogen adsorption and desorption for sample Al_2O_3, CCA03 and CCA03-2

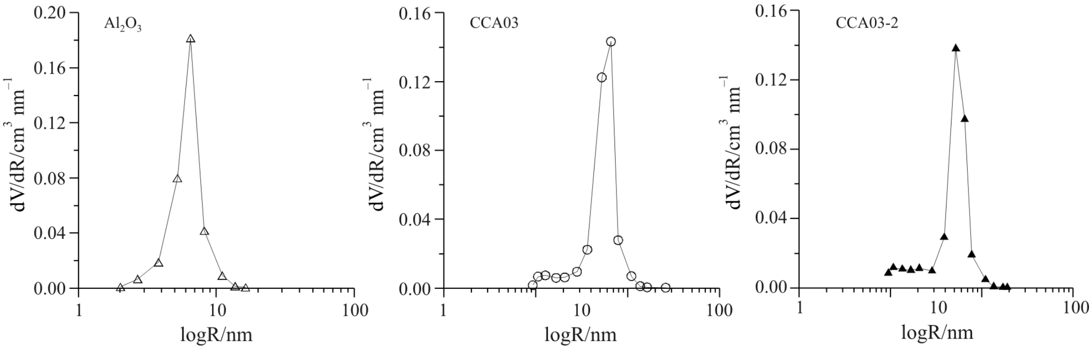

Fig. 4 Pore size distributions of sample Al_2O_3, CCA03 and CCA03-2

Table 1 Change of adsorption-structural parameters of alumina materials

Sample	SBET/ m^2 g^{-1}	Carbon content/ mass%	S_{MICRO}/ m^2 g^{-1}	$V_{(ads)BJH}$/ cm^3 g^{-1}	$V_{(DES)BJH}$/ cm^3 g^{-1}	V_{MICRO}/ cm^3 g^{-1}	D_{AV}/ nm
Al_2O_3	128	–	8.19	0.48	1.48	0.003	15
CCA03	166	5.7	6.17	0.50	0.49	0.002	12
CCA03-2	171	9.6	16.72	0.43	0.41	0.006	10

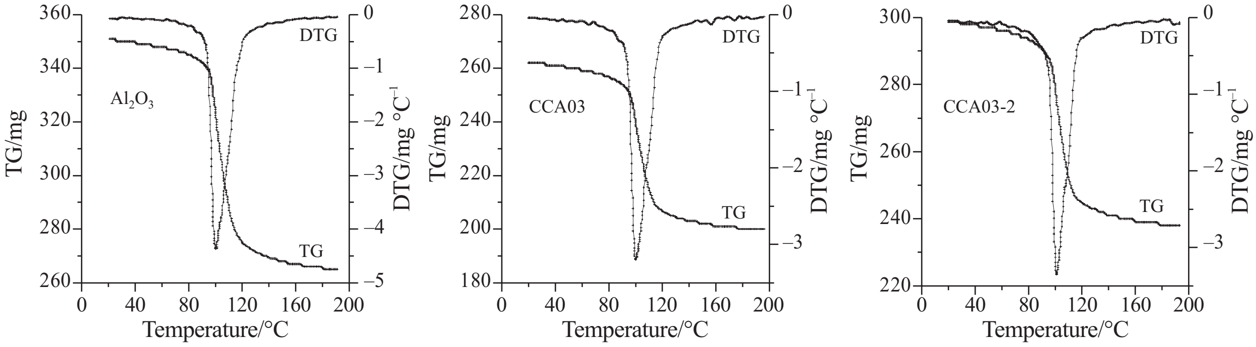

Fig. 5 Thermodesorption of water from the studied sample surfaces under the quasi-static conditions

liquid/alumina material systems, is characterized by wide range of application, high selectivity and resolution.

Figure 5 presents the exemplary measurement curves of liquid thermodesorption from the surface of studied samples. The Q-DTG curves describe the energetic state if liquid molecules on the surface of pure and modified alumina materials. The energy of interactions between molecules depends on the kind of adsorbate, properties of the surface on which they are adsorbed and porosity of the sample (presence of meso- and micropores). The differential DTG curves are characterized by the presence of one distinct peak. This is the evidence for continuity of thermodesorption and monotonic change of adsorption layer properties depending on the distance from the liquid molecule surface, which are bounded with the surface by the forces of different power and reach. In subsequent stages of sample desorption, adsorption liquid layers (range of capillary condensation) remaining in the reach of surface forces and form active surface sites are removed. Liquid adsorption with active sites on the surface depends on bonds of the same type.

Amounts of liquid vapour calculated for 1 mg of dry adsorbent decrease as following: Al_2O_3>CCA03>CCA03-02. Only the sequence for butanol vapour is different: CCA03> CCA03-02>Al_2O_3. To show these relationships the percentage mass loss curves of the liquids relate to temperature from the studied sample surfaces are presented in Fig. 6.

The method of programmed liquid thermodesorption from the surface of studied solids can be used for calculation of desorption energy and presentation of the desorption energy distribution function in a graphical form (Fig. 7) [2, 3].

Table 2 presents the ranges of E_d value changes for individual systems. Energy distribution functions differ in values, which indicates a complex mechanism of desorption, and effect of modification process. The higher values of distribution function are, the more active sites of a given energy on the surface of a solid. Increase in the value E_{dmax} indicates in-

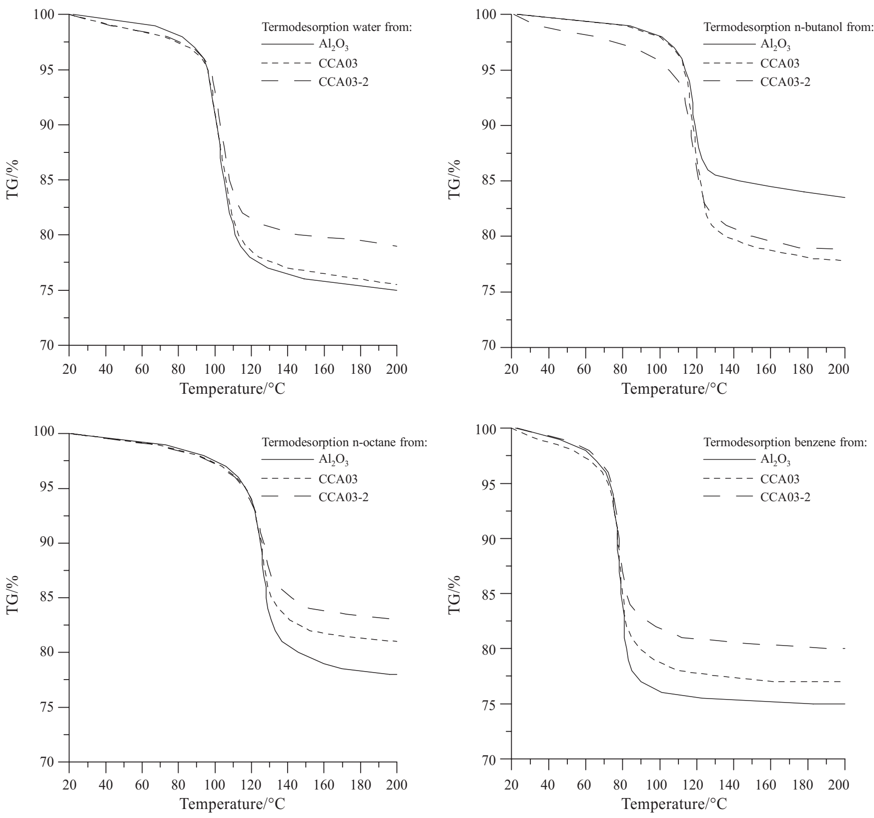

Fig. 6 Percentage mass losses of the liquids from the studied sample surfaces under the quasi-static conditions

Table 2 Comparison of desorption energy ranges for individual materials

Sample	Benzene		*n*-Octane		*n*-Butanol		Water	
	ΔEd	$Ed_{\max}$	ΔEd	$Ed_{\max}$	ΔEd	$Ed_{\max}$	ΔEd	$Ed_{\max}$
Al_2O_3	52	43	45	41	35	41	46	44
CCA03	39	38	55	37	50	44	46	39
CCA03-2	38	35	40	34	35	36	35	38

creasing adsorbent-adsorbate interactions. The shape of thermodesorption energy distribution function curves is similar to the Gauss curves with one distinct peak indicating the existence of one main active site on the surface of adsorbents. Values of desorption energy decrease as following: Al_2O_3>CCA03>CCA03-02. Only the sequence for butanol is different: CCA03>Al_2O_3>CCA03-02. Band broadening on the desorption energy distribution curves indicates increase of energetic heterogeneity of studied material. It is very well visible in the case of desorption energy distribution curves for Al_2O_3/water, benzene, *n*-octane systems and CCA03/butanol system.

Alumina and carbon-covered alumina are characterized by self-resemblance, which means that they can be decomposed into parts, which are geometrically similar to the whole. In other words, they are fractal objects. Thus fractal coefficients were used for structural estimation of these materials. They were calculated from the isotherms of low-temperature nitrogen adsorption and desorption by the methods based on the Frenkel, Halsey and Hill as well as Kisielev theory [4]. To compare the obtained values, additionally the fractal coefficients were determined by the independent methods using the data of programmed liquid thermodesorption from solid surfaces and the AFM data from The Scanning Probe Image Processor program [5–7]. The results are given in Table 3. The values of volumetric fractal coefficients from the sorptomatic measurements change in the range 2.49–2.66 which indicates heterogeneous distribution of pores. With the increasing D_f values, relative contribution of the pores of the values close to maximal increases. These data are well correlated with the surface fractal coefficients calculated based on the Fourier transformation from the AFM photos (from 2.42 to 2.63) and thermogravimetric method (from 2.34 to 2.58).

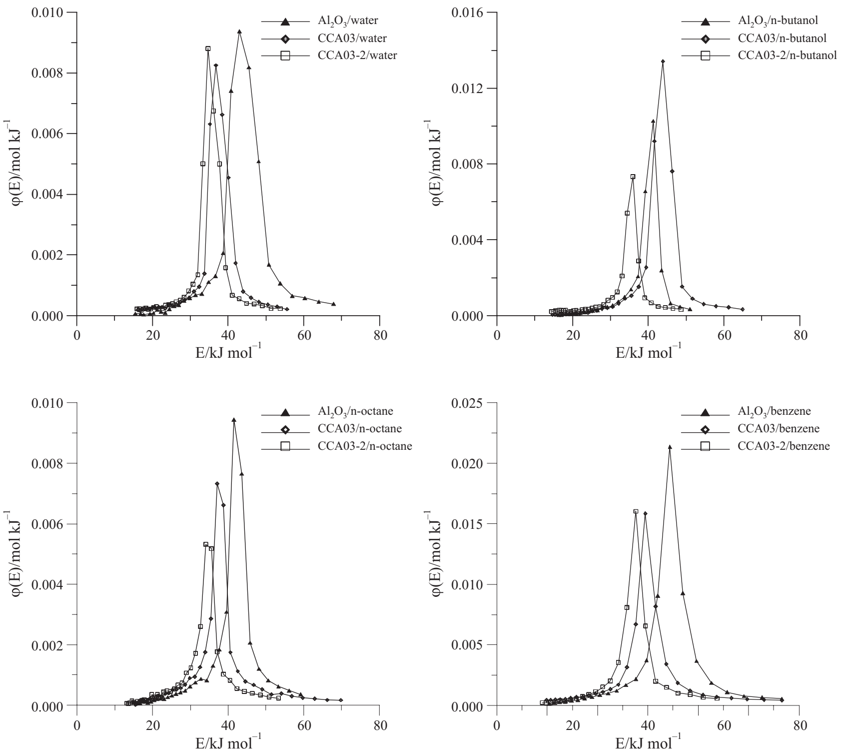

Fig. 7 Curves of water, butanol, *n*-octane and benzene desorption energy distribution from the samples

Table 3 Values of the volumetric and surface fractal coefficients

Sample	Sorptometric method			Thermogravimetric method				AFM method
	$D_{fv(1)}$	$D_{fv(2)}$	$D_{fv\ av.}$	Water	Butanol	*n*-Octane	Benzene	D_{fs}
Al_2O_3	2.49	2.66	2.57	2.55	2.46	2.34	2.44	2.54
CCA03	2.53	2.64	2.59	2.54	2.39	2.58	2.41	2.63
CCA03-2	2.54	2.59	2.57	2.44	2.43	2.49	2.45	2.42

Conclusions

Special applications of Q-TG thermal analysis for the investigation of adsorbed liquid layers and porosity parameters used for the quantitative characterisation of the energetic and geometrical (e.g. total) heterogeneities of alumina and carbon-covered alumina have been discussed. The presented method is very useful to investigate physicochemical properties of surface liquid films, adsorbate-adsorbent interactions and total nanotube surfaces heterogeneity. The thermodesorption process of liquids depends on the surface wetting phenomenon and surface properties of the solid surfaces.

The studies carried out using the above materials proved that the thermodesorption process takes place in a continuous way as evidenced by single inflexions on the Q-TG curves. They are a result of interactions in the adsorbate-adsorbent system and occurrence of one main active site.

Studies of low-temperature nitrogen adsorption confirmed that the values of specific surface area (S_{BET}) and total pore volume depend on size and structure of pure and modified alumina materials.

Comparison of the complex Q-TG, sorptometry and AFM data provide new information about the adsorption and structure of the studied materials.

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