

## THE INFLUENCE OF $Mn^{2+}$ AND $Ni^{2+}$ IONS ON THE SURFACE PROPERTIES OF THE ALUMINIUM OXIDE SAMPLES USING Q-TG AND Q-DTG DATA

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The paper presents the complex studies of adsorption and porosity of pure and modified–aluminium oxides samples. The presence of  $Mn^{2+}$  and  $Ni^{2+}$  modifiers on the aluminium oxide surface causes increase in water adsorption capacity and its decrease in the case of benzene and *n*-octane. This is due to decrease of specific surface area, volume and radius of pores as a result of surface impregnation and microcrystals formation during modification with manganese and nickel chlorides. Microcrystals formation on the surface and porosity decrease were confirmed by the AFM and SEM studies.

From the Q-TG and Q-DTG data, the energies of liquid desorption from the surface of the samples and the functions of desorption, energy distribution were calculated. High degree of nonlinearity of the run of the functions resulting from great heterogeneity of the studied surface was found. Adsorption of cations creates more homogeneous surface of aluminium oxide, and it is responsible for the change in adsorbate molecule interaction energy and changes mechanism of adsorption and desorption as well as thickness and structure of the adsorbed film. From the experimental data some parameters characterizing adsorption properties and porosity of the studied samples were determined using the measuring methods (thermal analysis, sorptomate, porosimetry, AFM).

**Keywords:** adsorption of ions, aluminium oxides, surface properties, thermal analysis

### Introduction

Chemical nature of active centres responsible for the phenomenon of adsorption is not yet completely known. Defects in the structure formed during dehydroxylation create active adsorption and catalytic centres. Various properties of aluminium oxide surfaces and the presence of different types of hydroxide groups of various concentration enable modification using various methods. Thermal dehydroxylation is a single method for aluminium oxide surface modification. Physically bonded water is removed during sample drying and surface dehydroxylation takes place at high temperatures (about 1000°C).

Aluminium oxide surfaces are modified in order to be applied for separation of mixtures and as catalysts in many industrial processes. A main task is to increase selectivity of adsorption on the surface of individual compounds included in the mixture. A more complex way of changing properties of aluminium oxide surface is modification by addition of chemical compounds (modifiers) activating the desired active centres and deactivating those undesired. Addition of acids or bases affecting concentration and reactivity of surface hydroxide groups of aluminium oxide can serve as an example of

such surface modification [1]. Another method of aluminium oxide surface modification is addition of new functional groups on their surface.

To increase activity of aluminium oxide as the adsorbing substance or catalyst support, it is modified with such metal cations as e.g. Mn, Ni, Cr, Fe, Co. Physico-chemical properties of the new surface (e.g. adsorption capacity, porosity) differ significantly from the primary one [2, 3]. In such modification aluminium oxide (support) is subjected to the action of the solution including an active component, i.e. metal ions [4, 5]. Solution excess not bonded with the support is removed by evaporation and the support can be of different character. The solution can be adsorbed on the support surface forming surface complex of various types. Solution components can undergo ion exchange with surface groups or chemical reaction. Interaction forces can be relatively weak and adsorption of active component can have character of physical adsorption. Depending on the interaction type, the addition methods can be divided into adsorption, ion exchange and impregnation [6].

Catalyst preparation techniques for the above ways can be different. In the adsorption and ion exchange methods the solution after support saturation is filtered

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off and washed. In the impregnation method the catalyst precursor is prepared by evaporation of the solution from above the support. In the first case the amount of the active component is determined by adsorption capacity of the carrier surface or by concentration of the solution, whereby some amount of solution can be closed in the support pores giving active component crystals after evaporation. Recognition of impregnation, adsorption from solution or ion exchange methods is not easy due to the fact that interaction of the adsorbate with the surface can be of different character in different parts of the same support. The term 'impregnation' is often used in practice as common for all methods of spreading the active component from the solution. The mechanism of nickel ions reaction with aluminium oxide is as follows. Nickel ions included in the solution react with aluminium oxide forming nickel–aluminium spinel  $\text{NiAl}_2\text{O}_4$  according to the reaction [7]:



Spinel formation for the  $\eta$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  species is observed at lower temperatures than for  $\alpha$ - $\text{Al}_2\text{O}_3$  ( $>100^\circ\text{C}$ ) [8]. In adsorption of ionic complex from their aqueous solution on aluminium oxide surfaces, the essential parameter determining adsorption capacity is the isoelectric point, *I.P.* that is the zero charge point. Oxide in the contact with the solution whose pH is below *I.P.* is positively polarized and surrounded by anions compensating this charge. However, it is negatively polarized adsorbing cations in contact with the solution of pH higher than *I.P.* Knowing the value of isoelectric point, it is possible to determine roughly the type of metal, anion or cation complex to be chosen for a given oxide – support and range of pH to be used during spreading. For aluminium oxide (*I.P.*=8) adsorption condition is the anion precursor of pH lower than 8 or the cation precursor of pH higher than about 8. The amount of active component which can be spread on the support surface, *M*, depends on many parameters: nature and structure of support, chemical properties of active component in the solution and spreading conditions. It can be written that:

$$M = f(\alpha, t, R, S, r_{\text{av}}, V_p, c, T, D_{\text{eff}}, \eta, \delta, \theta, \rho) \quad (2)$$

where  $\alpha$  – the parameter characterizing chemical properties of the spread compound and support surface, *t* – the time of interaction with the solution, *R* – the grain radii, *S* – the grain pore surface,  $r_{\text{av}}$  – the average pore radius,  $V_p$  – the volume of support pores, *T* – the temperature, *c* – the concentration of the spread component in the solution,  $D_{\text{eff}}$  – the effective diffusion coefficient,  $\eta$  – the solution viscosity,  $\delta$  – the surface tension,  $\theta$  – the angle of contact,  $\rho$  – the coefficient of meniscus curvature in pores.

The paper presents the results of studies on the effect of  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  cations on adsorption and catalytic

properties of the surfaces of aluminium oxides with respect to applicability in various technological processes. The analysis of physicochemical properties of modified aluminium oxide was made from the experimental results obtained by means of derivatograph, sorptometer as well as AFM and SEM microscopes. The special effort was made to estimate adsorption abilities of the samples for apolar and polar substances (water, benzene, *n*-octane) and surface porosity.

## Experimental

### *Methods, apparatus and materials*

Studies of liquids thermodesorption from the sample of commercial aluminium oxide (type Aldrich, USA) were carried out using a derivatograph Q-1500D (MOM Hungary) [8]. The Q-TG mass loss curve and Q-DTG differential mass loss curve in relation to temperature and time were measured under quasi-isothermal conditions over a 20–300°C temperature range. The curves were measured over a constant heating rate of 6°C min<sup>-1</sup> because optimal parameter. The sample was thermally treated in air in 300°C already located in the vacuum desiccator, where the relative vapour pressure of benzene was  $p/p_0=1$ . About 0.5 g of the wetted alumina oxide was placed in the special platinum crucible of the thermogravimetric analyzer.

Specific surface areas and pore volumes were determined from low-temperature nitrogen adsorption (Sorptomat Micrometrics ASAP 2405 V1.01, USA) and Porosimeter 4000 (Carlo Erba Instruments, Italy). The photographs were made by means of the atomic force microscopy NanoScope III (Digital Instruments, USA) and scanning electron microscope type BS-301 (Tesla).

The samples to be activated basic aluminium oxide produced by Aldrich were used for modification and then in the programmed thermodesorption. Its characteristics are presented in Table 1. The samples

**Table 1** Characteristics of the studied aluminium oxide provided by Aldrich

Activity in Brockman	I
Size of molecules/mesh	~150
Size of pores/Å	58
Specific surface area/m <sup>2</sup> g <sup>-1</sup>	155
Water/%	1.5
Na <sub>2</sub> O/%	0.4
Fe <sub>2</sub> O <sub>3</sub> max/%	0.02
SiO <sub>2</sub> max/%	0.02
No. of category	19.944-3
Type	Basic
PH	9.5±0.5

of active, basic aluminium oxide were subjected to the action of solutions containing various concentrations of metal ions ( $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ). The choice of these cations was not accidental. Modified samples with cations is used in industry as the adsorbent or catalyst in hydrogenation reactions and to separate gaseous mixtures like e.g.  $\text{H}_2/\text{Ar}$  [9, 10]. The samples of aluminium oxide modified with ions are used as chromatographic column packings, for separation of alkenes and alkanes [11].

The samples to be studied were prepared using the impregnation method [6] consisting in spreading the active component from the solution. Active, basic aluminium oxide was sieved and then the fraction of 0.15 nm grain thickness was removed. Hydrated manganese chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , analytical pure, POCH Gliwice) and hydrated nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , analytical pure, POCH Gliwice) were used for modification. Five 10 g portions of aluminium oxide were weighed and then placed in evaporating dishes. Then aqueous solutions of modifiers were prepared weighing a suitable amount of manganese and nickel salts so as to obtain the following molar concentrations: 0.05; 0.1; 0.2; 0.3 and 0.4  $\text{mmol g}^{-1}$  the weighed portions of salts were dissolved in 15 mL distilled water and then 10 g portions of aluminium oxide placed in the evaporating dish were dipped in succession. The evaporating dishes with the contents were heated with infrared searchlight while stirring to the complete evaporation of water. The obtained dry adsorbent was roasted at 400°C in the muffle furnace for 4 h. The contents of manganese chloride in five samples were: 0.99, 1.94, 3.81, 5.6 and 7.34% respectively, but in the samples modified with nickel chloride 1.17, 2.32, 4.54, 6.66 and 8.68%.

Distilled water, benzene (POCH Gliwice) and *n*-octane (analytically pure, Fluka) were used for adsorption from the gaseous phase on the surface of modified aluminium oxide samples. Before measurements of thermodesorption, the samples were prepared as follows. Suitable weighed portions of aluminium oxides were dried in the furnace at 300°C for 24 h to remove hygroscopic water from their surface. Then they were placed in the vacuum desiccator containing the studied liquid where  $p/p_0=1$  and left for 24 h to establish the adsorption equilibrium. Then the samples were subjected to programmed thermodesorption measurements in the temperature range 20–300°C. The obtained results of studies of the samples with spread manganese and nickel cations were compared with analogous parameters (e.g. adsorption capacity, pore volume, surface area, fractal dimensions) obtained for the sample of pure aluminium oxide.

The curves of thermodesorption Q-TG and Q-DTG of the above mentioned liquids from the surface of indi-

vidual aluminium oxide samples were recorded. From the obtained thermodesorption curves and data from the sorptomate (specific surface area size), the statistical number of liquid monolayers on the surface of studied aluminium oxides was calculated. The following dependence was used for calculations:

$$n = (a/S) k \quad (3)$$

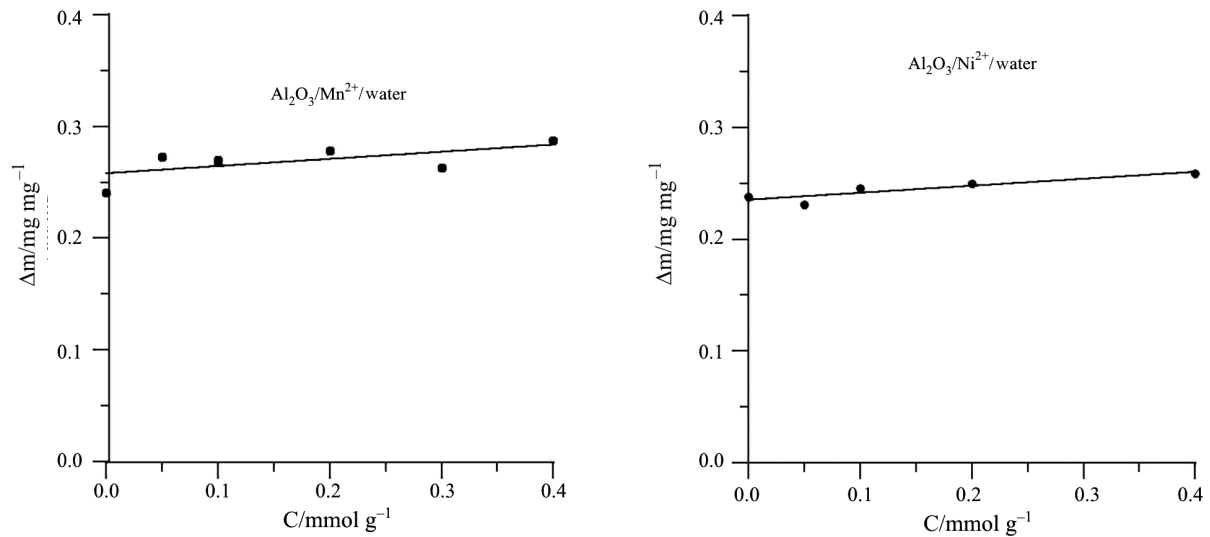
where  $n$  – the number of monolayers of the studied liquid,  $a$  – the amount of adsorbed liquid on the surface of the studied adsorbent (expressed in  $\text{mmol g}^{-1}$ ),  $S$  – the specific surface area of the studied adsorbent (expressed in  $\text{m}^2 \text{g}^{-1}$ ),  $k$  – the constant value characteristic of a given liquid dependent on the surface size occupied by one molecule (the value of  $k$  is 88.25, 210 and 254.8  $\text{Å}^2$  for water, benzene and *n*-octane, respectively, taken from paper [12]).

The properties of aluminium oxide sample surfaces modified with manganese and nickel cations were determined from the programmed thermodesorption data of some liquids (water, benzene and *n*-octane) using the so-called quasi-isothermal program of derivatograph Q-1500 D. Before studies the samples were saturated with liquid vapours in the vacuum desiccator where  $p/p_0=1$ . During such samples preparation before measurements, all surface forces were compensated by adsorbing liquid molecules.

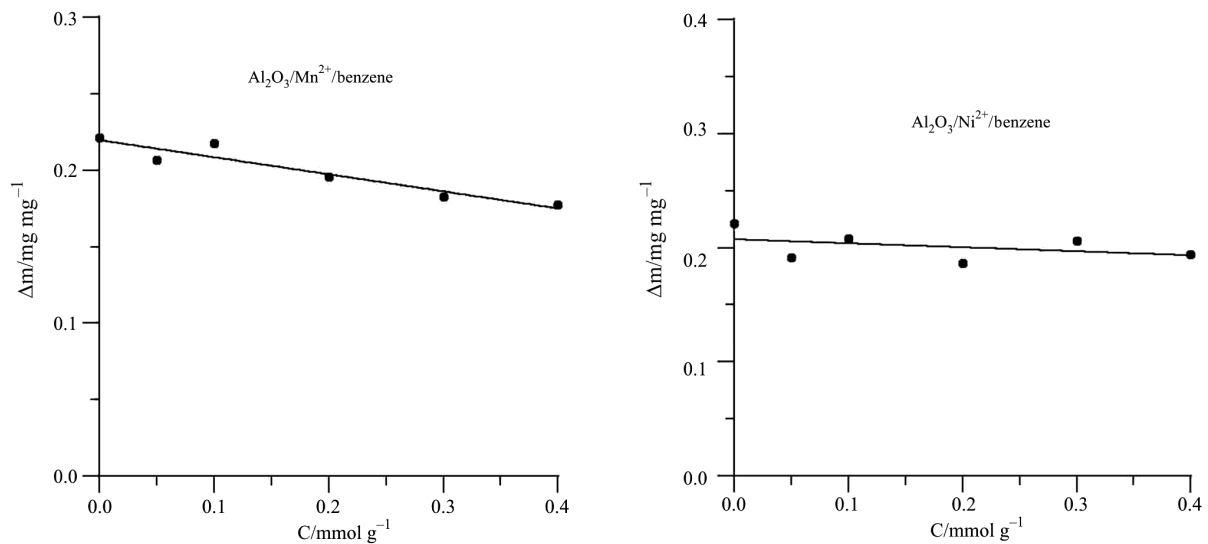
## Results and discussion

The calculated values of mass loss  $\Delta m$  corresponding to the sample adsorption capacity for individual liquids obtained from the measurements of thermal analysis are presented in Figs 1, 2 and 3 depending on the amount of the modifier  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  on the aluminium oxide surface. The curves of the dependence  $\Delta m=f(c)$  in these figures are very similar. In the case of water adsorption the value of sample adsorption capacity increases with the concentration of modifiers. However, the presence of cations on the surface decreases adsorption capacity of aluminium oxide compared with that of benzene and *n*-octane.

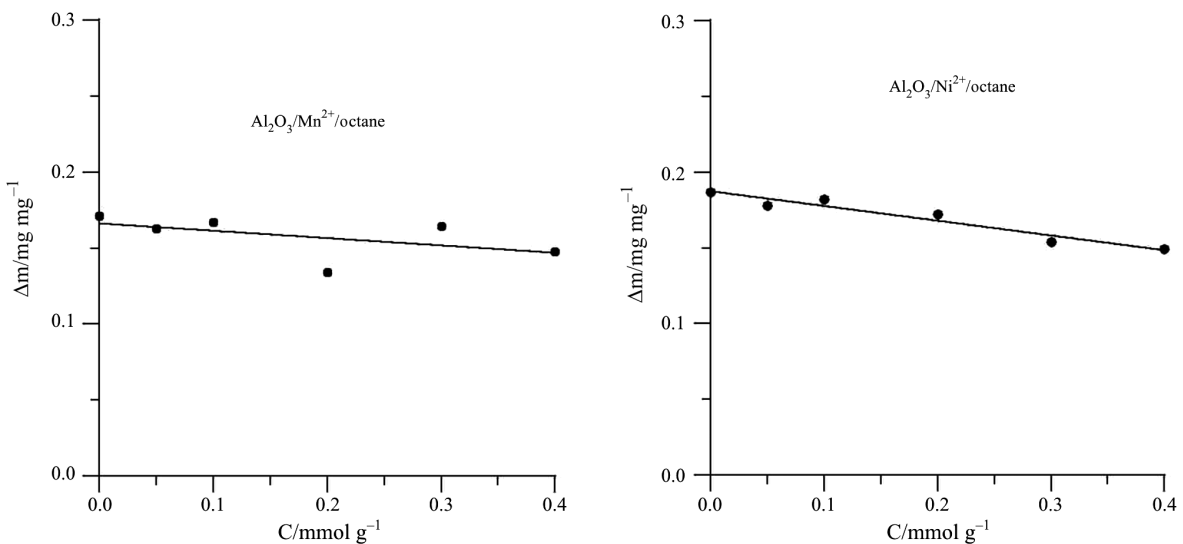
The greatest changes of values of water adsorption capacity ( $\Delta m$ ) were obtained for the samples of aluminium oxide with spread  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  cations of concentration  $c=0.4 \text{ mmol g}^{-1}$  (Fig. 1). For the samples with adsorbed benzene and *n*-octane on aluminium oxide (Figs 2 and 3), a tendency for decreasing of the amount of the liquid adsorbed on the surface of modified adsorbent (adsorption capacity  $\Delta m$ ) was observed. Therefore further parts of this chapter will describe the results of studies for the samples of aluminium oxide with spread cations of concentration  $0.4 \text{ mmol g}^{-1}$  which are responsible for the greatest



**Fig. 1** Dependence of adsorption capacity on the amount of the modifier  $Mn^{2+}$  and  $Ni^{2+}$  on the aluminium oxide with water



**Fig. 2** Dependence of adsorption capacity on the amount of the modifier  $Mn^{2+}$  and  $Ni^{2+}$  on the aluminium oxide with benzene



**Fig. 3** Dependence of adsorption capacity on the amount of the modifier  $Mn^{2+}$  and  $Ni^{2+}$  on the aluminium oxide with *n*-octane

changes in physicochemical properties of aluminium oxide surface.

The curves of liquid mass loss, Q-TG, and their differential curves, Q-DTG, are presented in Fig. 4 for pure samples and those covered with modifying substances (manganese and nickel chlorides of the solutions with concentrations  $0.4 \text{ mmol g}^{-1}$ ). They are characterized by occurrence of inflexions or peaks due to gradual evaporation of liquid depending on energy of molecule bonding in the adsorption layer with the surface of the studied sample. High sensitivity of the apparatus as well as selectivity and resolving power of individual inflexions or peaks on the curves Q-TG and Q-DTG obtained for the samples saturated in the desiccator compared with the samples completely wetted with the studied liquid, until the volumetric phase appears over the surface, results from the absence of the substance added in excess on the surface. Molecules of liquids of the volumetric phase blanch off and screen the effect of surface forces of active centres on the adsorbed molecules in adsorption layer. Covering of the surface with modifiers is responsible for occurrence of inflexions on the Q-DTG curves and shift of peak minima towards higher temperatures which is a result of increase of intermolecular interaction force and energy of liquid desorption from the surface of studied samples.

Table 2 presents the calculated values obtained from thermal analysis measurements for the above mentioned samples, the values of individual adsorption parameters (adsorption capacity,  $a$  expressed in  $\text{mmol g}^{-1}$  and the number of statistical liquid monolayers,  $n$ ).

From the curves Q-TG and Q-DTG there were determined the functions of energy distribution of liquid desorption from the surface of studied samples for individual liquids using the method described in papers [8, 9]. Estimation of surface energetic heterogeneity is based on condensation approximation applied

for description of desorption kinetics under the non-isothermal conditions (quasi-isothermal). The function of desorption energy distribution,  $\rho_n(E)$  can be calculated from the curves Q-TG and Q-DTG describing desorption kinetics [8]:

$$-\frac{1}{1-\theta_i} \frac{d\theta_i}{dT} = \frac{v_i}{\beta} \exp\left(-\frac{E_i}{RT}\right) \quad (4)$$

where  $T=T_0+\beta t$ ,  $\theta$  – the degree of surface coverage,  $v_i$  – the entropy coefficient,  $E_i$  – the desorption energy calculated for a given temperature  $i$ ,  $T_0$  and  $T$  – the initial and given temperature of desorption,  $\beta$  – the rate of sample heating,  $t$  – the time of process,  $R$  – the gaseous constant.

Final expression for calculating the function of desorption energy distribution  $\rho_n(E)$  can be written as follows:

$$\rho_n(E) = -\frac{d\theta}{dT} \frac{1}{T} \quad (5)$$

Equation (5) was used for calculating the function of desorption energy distribution of water, benzene and  $n$ -octane from the aluminium oxide surface modified with cations for a given temperature  $T$  from the curves Q-TG and Q-DTG. From the experimental data in Fig. 4 and using the above dependence there were calculated and plotted the functions of desorption energy distribution presented in Fig. 5 for the individual studied systems.

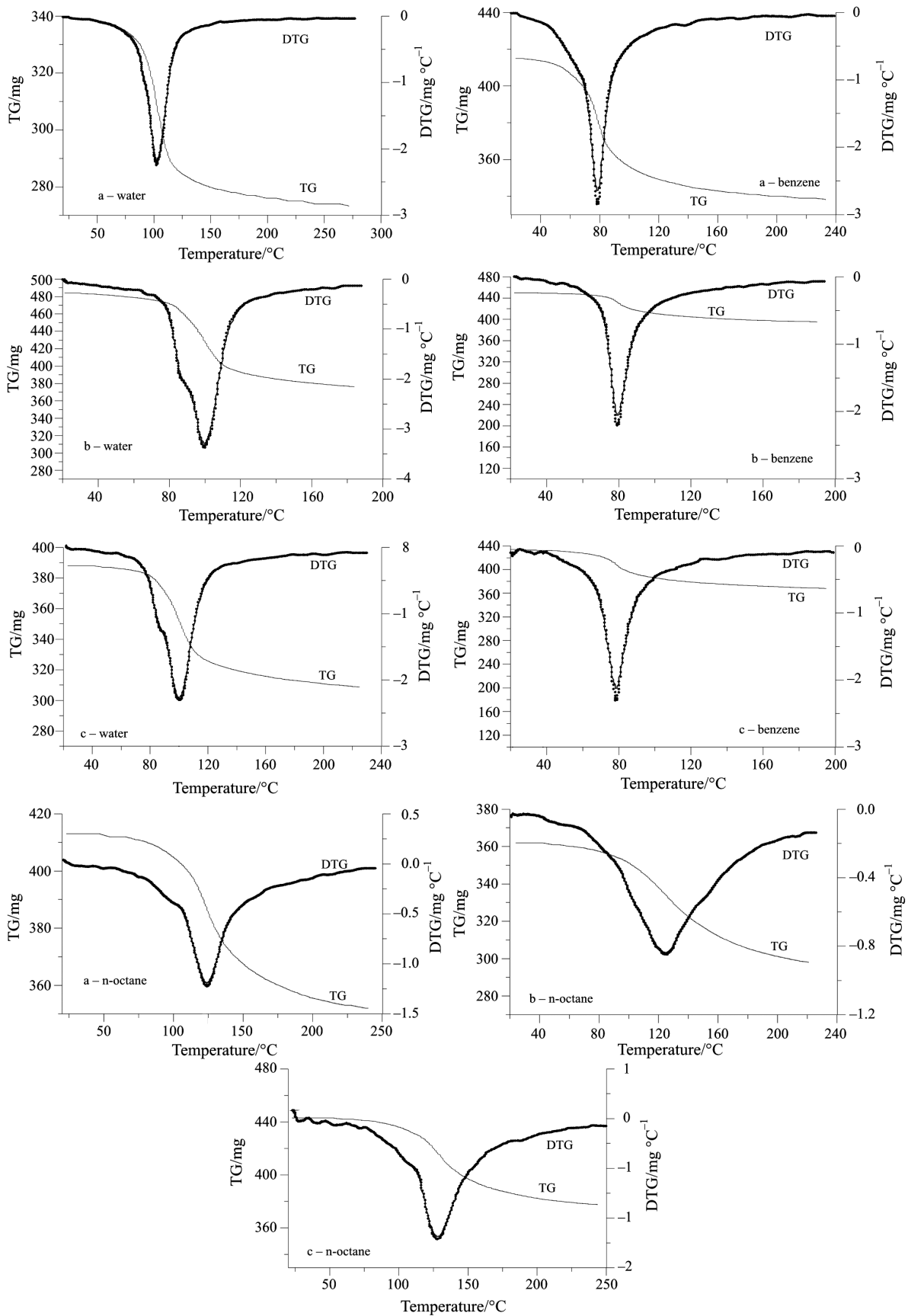
High degree of non-linearity of the above curves of the dependences calculated from Eq. (5) results from large energetic heterogeneity of the surface of studied samples. Table 3 presents the values of parameters describing energetic heterogeneity for the individual studied samples: range of changes in the desorption energy  $\Delta E_d$  (in  $\text{kJ mol}^{-1}$ ), values of desorption energy corresponding to the peak maximum,  $E_d^{\max}$  (in  $\text{kJ mol}^{-1}$ ) and maximal values of the

**Table 2** Properties of liquid adsorption layers on the surface of pure  $\text{Al}_2\text{O}_3$  and after modification samples

Samples	$a_{\text{water}}/\text{mmol g}^{-1}$	$n_{\text{water}}$	$a_{\text{benzene}}/\text{mmol g}^{-1}$	$n_{\text{benzene}}$	$a_{n\text{-octane}}/\text{mmol g}^{-1}$	$n_{n\text{-octane}}$
Pure $\text{Al}_2\text{O}_3$	13.5	5.85	2.57	3.12	1.51	2.2
$\text{Mn}^{2+}/\text{Al}_2\text{O}_3$	14.8	6.88	2.05	2.57	1.26	1.94
$\text{Ni}^{2+}/\text{Al}_2\text{O}_3$	13.8	6.21	2.39	3.02	1.36	2.09

**Table 3** Changes of desorption energy of the liquids from the tested samples

Samples	Water			Benzene			$n$ -Octane		
	$\Delta E_d/\text{kJ mol}^{-1}$	$E_d^{\max}/\text{kJ mol}^{-1}$	$\rho^{\max}/\text{mol kJ}^{-1}$	$\Delta E_d/\text{kJ mol}^{-1}$	$E_d^{\max}/\text{kJ mol}^{-1}$	$\rho^{\max}/\text{mol kJ}^{-1}$	$\Delta E_d/\text{kJ mol}^{-1}$	$E_d^{\max}/\text{kJ mol}^{-1}$	$\rho^{\max}/\text{mol kJ}^{-1}$
pure $\text{Al}_2\text{O}_3$	15–100	45	6.0	18–100	34	7.9	12–71	25	3.2
$\text{Al}_2\text{O}_3/\text{Mn}^{2+}$	44–59	52	8.6	53–71	59	7.5	31–41	38	2.6
$\text{Al}_2\text{O}_3/\text{Ni}^{2+}$	47–62	53	6.5	53–70	57	7.3	20–27	25.5	3.5



**Fig. 4** The Q-TG and Q-DTG curves of liquid thermodesorption from the surfaces: a – pure  $\text{Al}_2\text{O}_3$ , b – modified with  $\text{Mn}^{2+}$ , c – modified with  $\text{Ni}^{2+}$

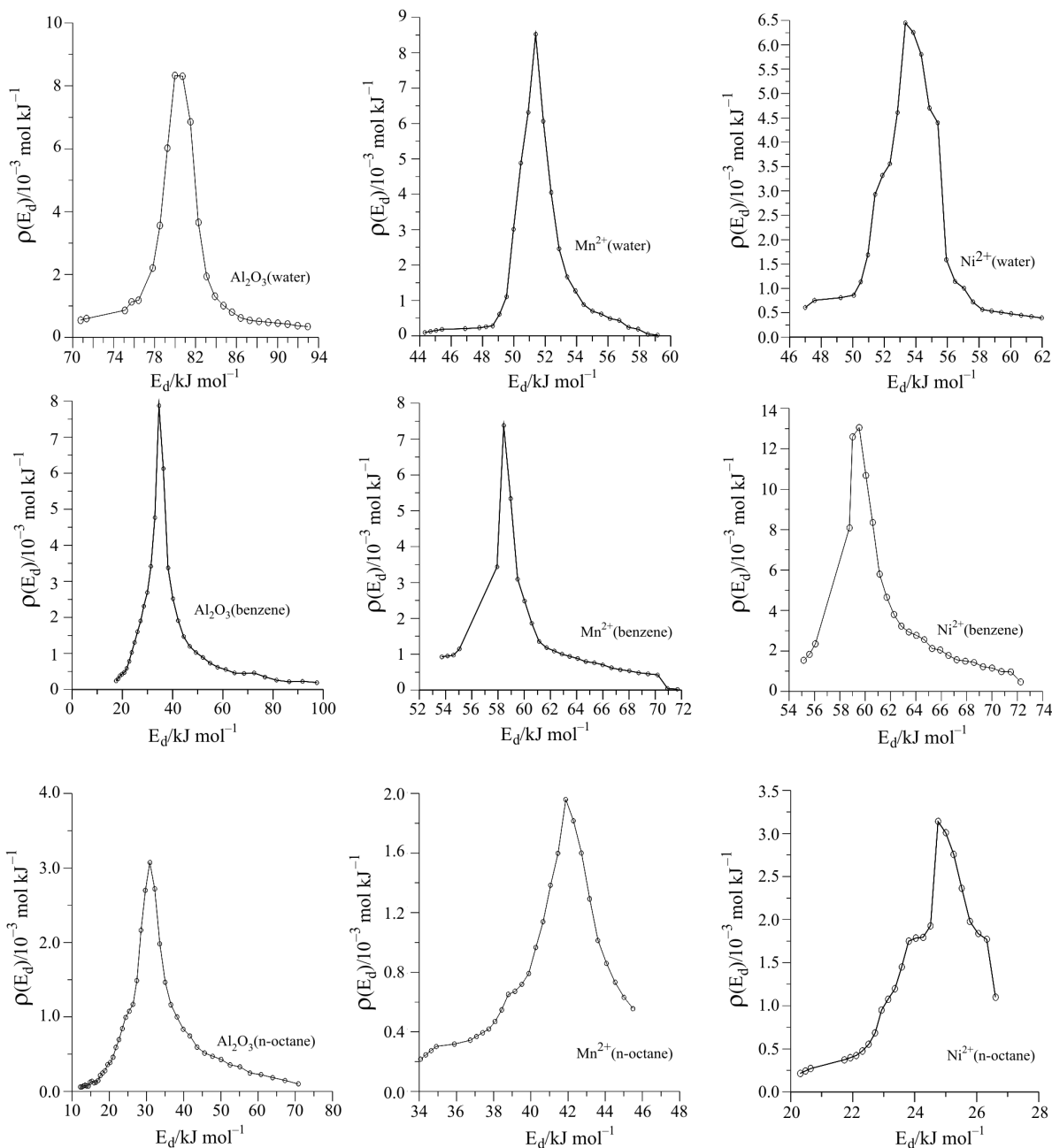


Fig. 5 Energy distribution function of liquids desorption from modified and unmodified  $\text{Al}_2\text{O}_3$  samples

derivative of the number of active centres after the energy  $\rho^{\max}$  (in  $\text{mol kJ}^{-1}$ ). The functions of desorption energy distribution of the samples modified with  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  ions differ in size of desorption energy and shape of curves.

The presented calculations of desorption energy distribution function indicate a complex mechanism of desorption and an effect of ions on properties of aluminium oxide surface. In the case of water adsorption there is observed shift of desorption energy value corresponding to the peak maximum ( $E_d^{\max}$ ) on the distribution curve towards higher values  $E_d$ , for the samples with spread modifiers. This can be due to the

effect of adsorbed cations on the aluminium oxide surface on the properties of water layer bonded with the surface. Cations cause formation of a new structure of adsorption layer responsible for the increase of its thickness, but thickness decreases for benzene and *n*-octane. Similar dependences of adsorption energy changes are found for other liquids (benzene, *n*-octane) whereby the value  $E_d$  for the sample with adsorbed *n*-octane is about 1.5 times as large as that for the sample  $\text{Mn}^{2+}/\text{Al}_2\text{O}_3$ , compared with the pure sample  $\text{Al}_2\text{O}_3$ . This is due to stronger interaction of *n*-octane molecules with new active centres on the surface

**Table 4** Adsorption and structural parameters of the pure and modified aluminium oxide determined from the nitrogen adsorption isotherms

Samples	Pore diameter, $R/\text{nm}$			Total pore volume, $V/\text{cm}^3 \text{g}^{-1}$			Specific surface area, $S/\text{m}^2 \text{g}^{-1}$
	methods			Single point	BJH (ads.)	BJH (des.)	BET method
	BET	BJH (ads.)	BJH (des.)				
Pure $\text{Al}_2\text{O}_3$	5.82	4.81	4.16	0.25	0.27	0.27	174.9
$\text{Mn}^{2+}/\text{Al}_2\text{O}_3$	5.78	4.68	4.07	0.24	0.25	0.25	164.3
$\text{Ni}^{2+}/\text{Al}_2\text{O}_3$	5.76	4.68	4.05	0.24	0.25	0.25	167.6

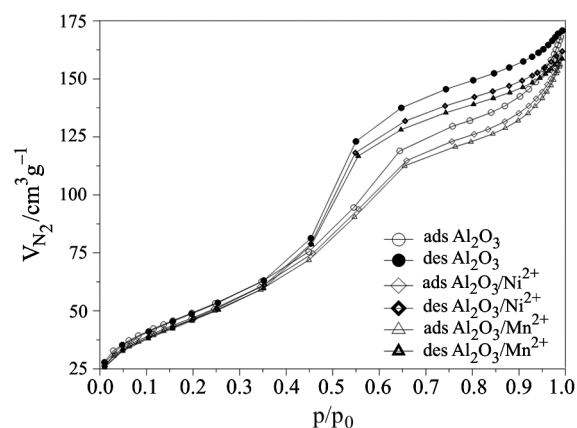
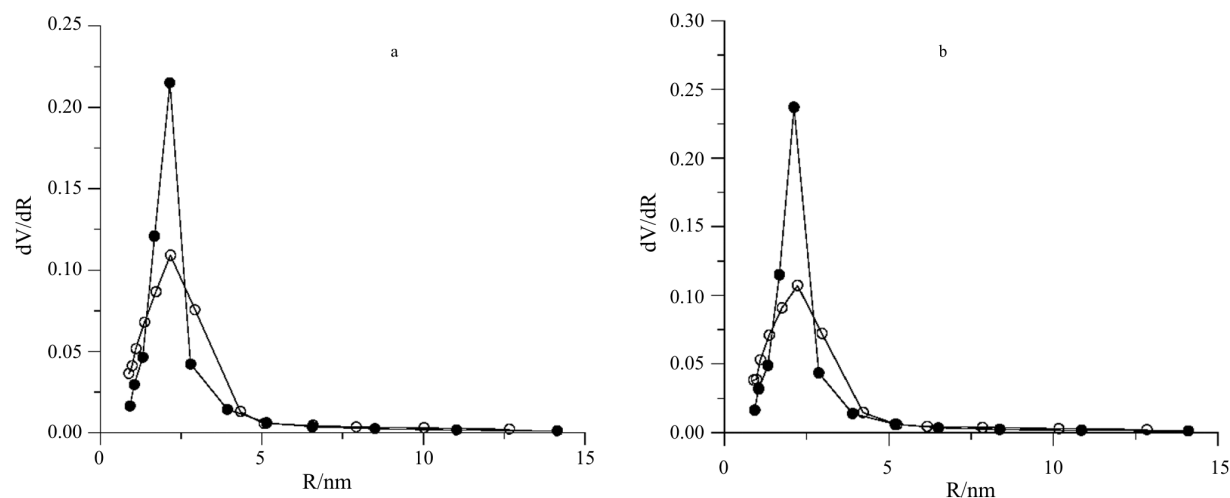
(formation of a new structure, stiffening of adsorption film of smaller thickness).

These differences are caused by formation of new, energetically different active centres by ions affecting the mechanism of adsorption and desorption processes as well as properties of adsorption layers (thickness, structure). After modification with manganese and nickel chlorides, the aluminium oxide surface becomes more homogeneous probably due to formation of microcrystals. Properties of the new surface are a result of the influence of manganese and nickel cat-

ions, as well chloride anions on adsorption properties and sample porosity. Modification of the surface with aluminium oxide cations reduces basic character of the adsorbent and changes adsorbate molecule interactions with its surface. However, adsorption of chloride anions masks Lewis active acidic centres (Table 2).

Parameters of porosity (i.e. geometric heterogeneity) of the studied samples included in Table 4 were calculated from the adsorption–desorption isotherms of nitrogen (Fig. 6), obtained by means of sorptomate which can be classified as type II according to BET. This type of curves results from a polymolecular adsorption layer of nitrogen. The presence of hysteresis loop on the adsorption–desorption isotherms is the evidence for the capillary condensation phenomenon. As follows from Table 4 the specific surface area size calculated using the BET method decreases in the case of modification with manganese and nickel cations which results from smaller adsorption of nitrogen (Fig. 6). The values of diameter and pore volume calculated from isotherms also decrease due to formation of manganese and nickel chloride microcrystals.

Figure 7 presents the functions of pore volume distribution in relation to their radii for the samples modified with manganese and nickel cations calculated from the low-temperature adsorption–desorption isotherms of nitrogen (Fig. 6). The presented curves have

**Fig. 6** Nitrogen adsorption–desorption isotherms for modified and unmodified  $\text{Al}_2\text{O}_3$  samples**Fig. 7** Pore-size distribution functions of  $\text{Al}_2\text{O}_3$  samples modified by a –  $\text{Mn}^{2+}$  and b –  $\text{Ni}^{2+}$



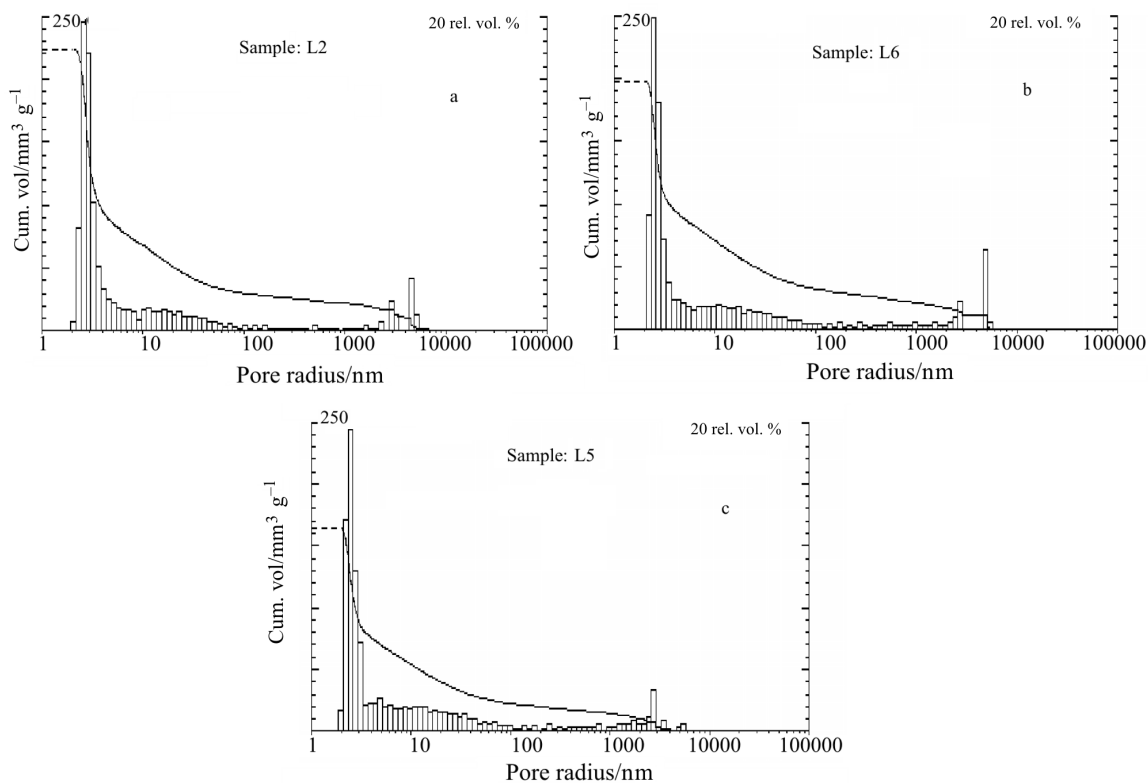


Fig. 8 Pore-size distribution functions for a – pure  $\text{Al}_2\text{O}_3$ , b – modified with  $\text{Mn}^{2+}$ , c – modified with  $\text{Ni}^{2+}$

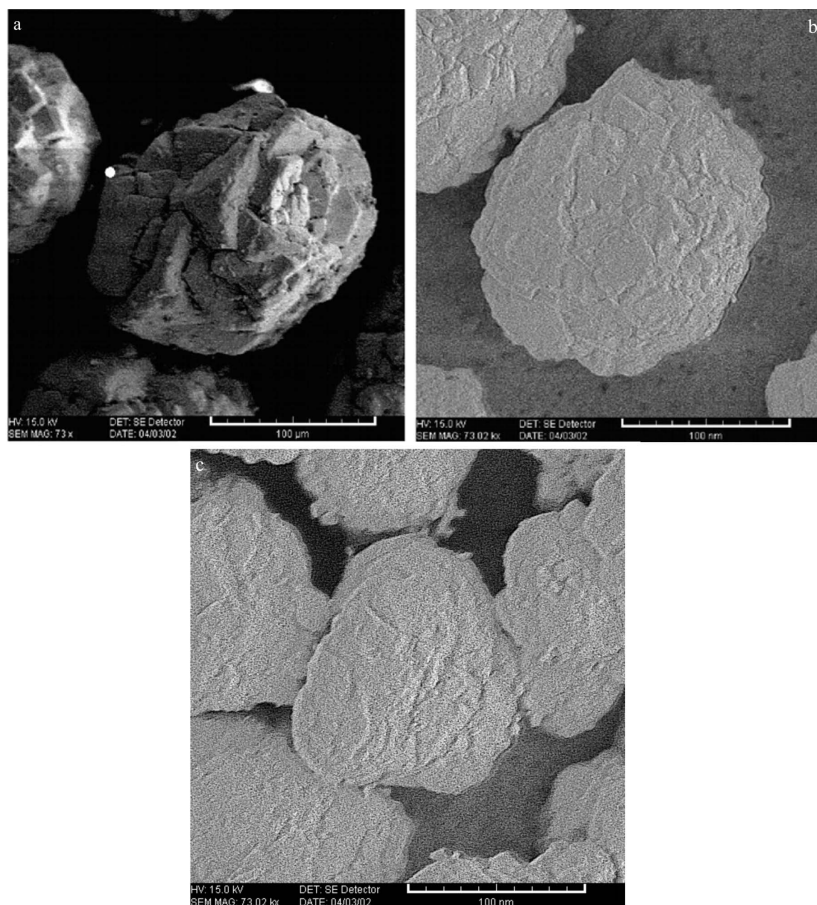


Fig. 9 SEM photographs of the sample surface: a – pure  $\text{Al}_2\text{O}_3$ , b – modified by  $\text{Mn}^{2+}$ , c – modified by  $\text{Ni}^{2+}$

**Table 5** Structural parameters of the pure and modified aluminium oxide samples determined from porosimetry method

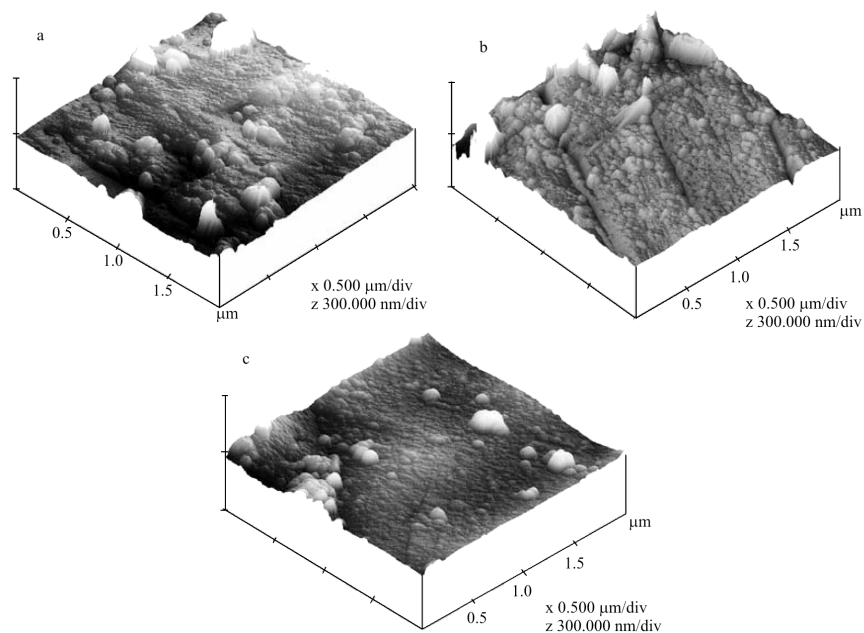
Samples	Pore diameter, $R/\text{nm}$	Total pore volume, $V/\text{cm}^3 \text{g}^{-1}$	Specific surface area, $S/\text{m}^2 \text{g}^{-1}$
pure $\text{Al}_2\text{O}_3$	3.2	0.22	107.5
$\text{Mn}^{2+}/\text{Al}_2\text{O}_3$	3.6	0.19	90.9
$\text{Ni}^{2+}/\text{Al}_2\text{O}_3$	3.2	0.16	81.7

**Table 6** The comparison of the obtained results of calculations with the data of measurements made by means of sorptometry and porosimetry methods (in  $\text{cm}^3 \text{g}^{-1}$ )

Samples	Thermodesorption of			Sorptometry: Single point, BJJ (ads.), BJJ (des.)	Porosimetry
	water	benzene	<i>n</i> -octane	volume of $\text{N}_2$	volume of Hg
pure $\text{Al}_2\text{O}_3$	0.25	0.25	0.28	0.25, 0.27, 0.26	0.22
$\text{Mn}^{2+}/\text{Al}_2\text{O}_3$	0.27	0.20	0.23	0.24, 0.25, 0.25	0.19
$\text{Ni}^{2+}/\text{Al}_2\text{O}_3$	0.26	0.23	0.26	0.24, 0.26, 0.25	0.16

**Table 7** Values of fractal dimensions (without unit)

Sample	Thermodesorption of			Sorptometry	Porosimetry	AFM
	water	benzene	<i>n</i> -octane			
Pure $\text{Al}_2\text{O}_3$	2.41	2.42	2.39	2.4	2.5	2.66
$\text{Mn}^{2+}/\text{Al}_2\text{O}_3$	2.39	2.42	2.38	2.39	2.4	2.52
$\text{Ni}^{2+}/\text{Al}_2\text{O}_3$	2.40	2.41	2.39	2.39	2.42	2.53

**Fig. 10** AFM photographs of the sample surface: a – pure  $\text{Al}_2\text{O}_3$ , b – modified by  $\text{Mn}^{2+}$ , c – modified by  $\text{Ni}^{2+}$ 

typical curve runs similar to Gauss ones with the peak maxima corresponding to the radii given in Table 4.

From the adsorption – desorption isotherms of nitrogen, fractal dimensions were calculated from the dependence [13, 14]:

$$D_f = 3 - d[\ln a(x)]/d[\ln(-\ln x)] \quad (6)$$

where  $a$  – the adsorption value,  $x = p/p_0$ .

For the studied samples the following values of fractal dimensions were obtained:  $D_f = 2.4$  for the samples with spread manganese and nickel cations the same value  $D_f = 2.39$ .

Thus the presence of a modifier (cation) on the surface causes insignificant decrease of fractal dimension due to increase in porosity of samples. Figure 8 show the functions of pore volume distribution to-

wards the radii of the above mentioned samples. Porosity parameters (diameter and pore volume as well as specific surface area size) are collected in Table 5 for the studied samples. Generally the trend of changes of these parameters is similar to those obtained by means of sorptometer (Table 4). However, numerical values of the obtained data are different in both standard methods which is obvious, among others, from the fact that the porosimetric method is the so-called destructive method for the studied sample.

Loss of liquid mass  $\Delta m$  from the samples during programmed thermodesorption was calculated into the volume occupied by the liquid in the pores of the studied material from the curves Q-TG. Table 6 presents the comparison of the obtained results of calculations with the data of measurements made by means of sorptometer and porosimetry. Comparison of the above data obtained from three independent measurement techniques gives good agreement.

Figure 9 shows the micrographs pictures of porous structure of samples obtained by scanning microscopy (SEM) as complementary to the qualitative presentation. As follows from the visual comparison, the surfaces after modification with cations are less porous (coarse) than pure surfaces, as confirmed by the studies made using a sorptometer and a porosimeter.

Figure 10 presents the images pictures of the porous structure of the samples of pure and aluminium oxide modified made using an atomic force microscope AFM. From the comparison of sample images, it also follows that the surfaces after modification with cations are less porous than the pure surface. From the AFM data the surface fractal dimensions were calculated. They are 2.60 (pure aluminium oxide), 2.52 (modified with manganese chloride) and 2.53 (modified with nickel chloride). The results presented in Table 6 confirm the studies of changes (decrease) of sample porosity after modification made by the use of derivatograph, sorptometer and porosimeter.

## Conclusions

On the basis of the obtained results it can be concluded that the presence of cations on the surface decreases adsorption capacity of aluminium oxide compared with that of benzene and *n*-octane. Adsorption capacity of water increases with the concentration of modifiers. The greatest changes of values of water adsorption capacity were obtained for the samples of aluminium oxide with spread  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  cations of concentration  $c=0.4 \text{ mmol g}^{-1}$ . These differences are caused by formation of new, energetically different active centres by ions affecting the mechanism of adsorption and desorption processes, as well as properties of adsorption layers (thickness, structure).

The functions of desorption energy distribution of the samples modified with  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  ions differ in size of desorption energy and shape of curves. High degree of nonlinearity of the above curves results from large energetic heterogeneity of the surface of studied samples of material. After modification with manganese and nickel chlorides, the aluminium oxide surface becomes more homogeneous probably due to formation of microcrystals. Properties of the new surface are a result of influence of manganese and nickel cations as well chloride anions on adsorption properties and sample porosity. The presence of a modifier (cation) on the surface causes insignificant decrease of fractal dimension due to increase in porosity of samples.

The comparison of the obtained results of calculations with the data of measurements made by means of complex methods was made. Comparison of adsorption and porosity parameters obtained from independent techniques gives good agreement.

## References

- 1 S. J. Teichner, *Bul. Soc. Chim. Fr.*, 7-8 (1974) 1226.
- 2 J. Deng, Z. Cao and B. Zhou, *Appl. Catal. A: General*, 132 (1995) 9.
- 3 M. N. Ramsis, Ch. A. Philip, M. Abd El Khlik and E. R. Souaya, *J. Thermal Anal.*, 46 (1996) 1775.
- 4 E. Kis, R. Marinkovic-Neducin, G. Lomic, G. Boskovic, D. Z. Obadovic, J. Kiurski and P. Putanov, *Polyhedron*, 17 (1998) 27.
- 5 D. Franquin, S. Monteverdi, S. Molina, M. M. Betahar and Y. Fort, *J. Mater. Sci.*, 34 (1999) 4481.
- 6 B. Grzybowska-Ćwierkosz, *Elementy katalizy heterogenicznej (Elements of heterogeneity catalysis)*, PWN, Warszawa 1993.
- 7 B. B. Popowski, *Nauka, (Novosibirsk)*, 61 (1976) 16.
- 8 D. Sternik, P. Staszczuk, G. Grodzicka, J. Pékalska and K. Skrzypiec, *J. Therm. Anal. Cal.*, 77 (2004) 171.
- 9 A. K. Khattak, M. Afzal, M. Saleem, G. Yasmeen and R. Ahmad, *Colloids Surf., A: Physicochem. Engin. Aspects*, 162 (2000) 99.
- 10 J. Deng, Z. Cao and B. Zhou, *Appl. Catal., A: General*, 132 (1995) 9.
- 11 A. Braithwaite and M. Cooper, *Chromatographia*, 429 (1996) 77.
- 12 A. L. McClellan and H. F. Harnsberger, *J. Coll. Int. Sci.*, 23 (1967) 577.
- 13 P. Staszczuk, V. V. Kutarov and M. Planda, *J. Therm. Anal. Cal.*, 71 (2003) 445.
- 14 P. Staszczuk, D. Sternik and V. V. Kutarov, *J. Therm. Anal. Cal.*, 69 (2003) 23.

Received: March 25, 2005

Accepted: June 10, 2005

OnlineFirst: January 11, 2006

DOI: 10.1007/s10973-005-7015-y