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## Conditions of the Formation and Properties of an Adsorbent Obtained from Aluminum Oxide Modified with Polyimide

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**Abstract**—The change in textural and chromatographic properties of separation layers obtained from aluminum oxide modified with polyimide is studied via low-temperature nitrogen adsorption, high-resolution transmission electron microscopy, and gas chromatography. The specific surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> adsorbent + 10 wt % polyimide falls from 228.9 to 190.4 m<sup>2</sup>/g with a slight increase in pore size from 83.6 to 86.5 Å upon thermal aging at 250 to 450°C in an inert gas flow. The uniform arrangement of carbon on the surface layers and almost Gaussian shape of the peaks of the components separated indicate a homogeneous adsorbent surface forms. This is achieved after removing active sites of sodium, iron, and titanium in the initial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, modifying its surface with polyimide, and thermal aging at 450°C. Carbon monoxide and carbon dioxide are selectively eluted from the associated permanent gases and hydrocarbons.

**Keywords:** gas chromatography, fluorinated polyimide, aluminum oxide, permanent gases, hydrocarbons

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### INTRODUCTION

Numerous studies in recent years have been aimed at developing inorganic gas separation membranes obtained from organic precursors and available inorganic materials. Aluminum and silicon oxides are used as inorganic supports, while phenolic and alcohol resins, polyvinylidene chloride, condensed polycyclic aromatic compounds, and polyimides act as organic precursors. Inorganic supports are impregnated with precursors and subjected to heat treatment in inert atmospheres at predetermined temperatures, and materials with specific properties are obtained.

Aromatic polyimides synthesized from monomers containing bulky CH<sub>3</sub> and CF<sub>3</sub> groups are of great interest. Polyimides with such structures have lower chain packing and thus greater permittivity and free volume in a polymer. In addition, aromatic polyimides form strong carbonized films during heat treatment at high temperatures. Materials obtained from polyimides and inorganic adsorbents (aluminum or silicon oxides) have porous structures, thermal stability, and chemical inertness, so they can be used as electrodes, membranes, and catalyst supports. They are also promising candidates for new chromatographic adsorbents [1–3].

The conditions of thermal aging significantly influence the selectivity and permeability of polyimide membranes. For example, the supports structurally

similar to carbon molecular sieves are obtained at 700°C.

Carbon molecular sieves are extensively used in gas chromatography to analyze permanent gases (nitrogen, oxygen, hydrogen, carbon monoxide, and methane) and light hydrocarbons. However, these adsorbents are currently expensive. It is therefore necessary to develop materials with similar properties based on freely available aluminum oxide.

The  $\gamma$ -form of aluminum oxide has long been used as an adsorbent in gas and thin-layer chromatography. The initial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is hygroscopic, and its activity depends on the amount of water and the active centers of sodium, iron, and titanium on the material's surface. It is recommended that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> be subjected to preliminary heat treatment or modified with either an organic liquid phase or inorganic salts to reduce the effect hydroxyl groups and metal atoms have on its capacity for separation [4, 5].

The adsorption and chromatographic properties of separation layers obtained from inorganic adsorbents (diatomite support or aluminum oxide) and perfluorinated polyimide synthesized by preparing polyamic acid (PAA) were studied in our earlier works. The surfaces of adsorbents with properties of nonpolar stationary phases, porous polymers, and molecular sieves formed when analyzing a mixture of constant gases and light hydrocarbons, depending on the tempera-

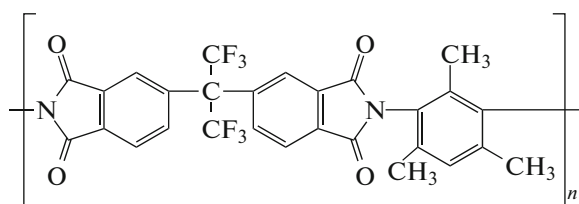


Fig. 1. Structural formula of PI-1B polyimide.

ture of thermal aging (250, 450, and 700°C) [6–10]. The components of this mixture were separated satisfactorily on a diatomaceous support modified with polyamic acid after it was aged in an inert gas flow at 700°C, but the resolution of the peaks of acetylene and ethylene was very poor [8–10]. Carbon dioxide was eluted from the surface of another support (aluminum oxide modified with PAA and heat aged at 450°C) with a tailing peak [7]. These disadvantages were probably due to the partial deformation or destruction of the polymer film that formed during the imidization of polyamic acid on the surface of the adsorbent and its heating, which resulted in a fairly inhomogenous surface. Polyamic acid has a higher adhesion to polar surfaces due to the presence acid groups. PAA solutions, however, are subject to hydrolysis when stored and applied to surfaces of inorganic materials. This leads to a decrease in the molecular weight of the polymer and a significant shrinkage of the polymer film during subsequent imidization.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> was impregnated with a solution of high molecular weight polyimide, the synthesis of which was described in [11]. Its structure was similar to one obtained via the imidization of polyamic acid to avoid the hydrolysis of PAA and obtain a uniform adsorbent surface. In addition, the active centers of sodium, iron, and titanium were preliminarily removed from the initial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

**Table 1.** Types of 3 m × 2 mm packed columns filled with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> + 10 wt % PI-1B

Columns	Initial $\gamma$ -Al <sub>2</sub> O <sub>3</sub> $T_{ag} = 90$ – $100^\circ\text{C}$	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> + 10 wt % PI-1B $T_{ag}, ^\circ\text{C}$
1	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> without HCl treatment	250
2		450
3	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> after HCl treatment	250
4		350
5		450

$T_{ag}$  is the temperature of thermal aging.

The aim of this work was to study the adsorption and chromatographic properties of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/polyimide adsorbents obtained after thermal aging at different temperatures.

## EXPERIMENTAL

### Reagents

In this work, we used 99% 2,4,6-trimethyl-*m*-phenylenediamine (2,4,6-TMmPDA) (Aldrich-Supelco) without further purification. In addition, 99% 2,2-bis(3,4-anhydrodicarboxyphenyl)hexafluoropropane (6FDA) (Aldrich-Supelco) was dried in vacuum for 6 h at 140°C before use.

Chemically pure dimethylacetamide (DMA) was used as a solvent (99.8%, Ekos-1). It was preliminarily purified via distillation over P<sub>2</sub>O<sub>5</sub> and stored over 5A molecular sieves (residual moisture, <0.02%).

PI-1B polyimide (Fig. 1) was synthesized from 2,4,6-trimethyl-*m*-phenylenediamine and 6FDA in a molten benzoic acid according to the procedure described in [11].

Chemically pure aluminum oxide  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Sasol Limited, South Africa) (product no. 608 114; Si, 0.015%; Fe, 0.015%; Ti, 0.015%; Na, 0.01%;  $S_{sp} = 200$ – $220$  m<sup>2</sup>/g), the fraction of which was 0.25–0.10 mm, was used as an inorganic adsorbent.

### Preparing the Adsorbent and Packed Columns

The crushed adsorbent was added to concentrated hydrochloric acid and left for 20 min to remove calcium, sodium, iron, and titanium ions. The adsorbent was then washed with distilled water to completely remove chloride ions and dried at 90–100°C.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was conditioned in a helium flow at 230–240°C and impregnated with polyimide preliminarily dissolved in dimethylacetamide (DMA).

PI-1B was dissolved in DMA in amounts of 10% of the adsorbent mass.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was then added, and the solution was held for 8 h. The suspension was poured into a porcelain cup and dried to constant weight at 90–100°C under constant stirring. The packed columns were then filled with the prepared adsorbent.

Table 1 shows individually packed columns prepared with the adsorbents and aged thermally in an inert gas flow at different temperatures for 10 h each.

Our adsorption studies were performed using the nitrogen adsorption–desorption isotherms at 77 K, which were measured on an ASAP-2400 device (Micromeritics, United States) after aging the samples in vacuum at 150°C. These isotherms were used to calculate the total surface with the Brunauer–Emmett–Teller technique and the total pore volume at a pressure of  $p/p_0 \sim 0.982$ – $0.983$ . The volume of micropores was calculated with the comparative  $t$  approach according to de Boer. The average diameter of pores

**Table 2.** Textural properties of adsorbents

Parameter	$\gamma\text{-Al}_2\text{O}_3$ without HCl treatment			$\gamma\text{-Al}_2\text{O}_3$ after HCl treatment			
	$\gamma\text{-Al}_2\text{O}_3$ init	10 wt % PI-1B		$\gamma\text{-Al}_2\text{O}_3$ init	10 wt % PI-1B		
$T_{\text{ag}}, ^\circ\text{C}$	250	250	450	250	250	350	450
$A_{\text{BET}}, \text{m}^2/\text{g}$	227.0	166.4	167.5	228.9	227.8	234.6	190.4
$V_{\text{por}}, \text{cm}^3/\text{g}$	0.54	0.31	0.34	0.53	0.55	0.56	0.53
$d_{\text{por}}, \text{nm}$ (according to BET)	7.8	7.4	7.4	9.0	8.8	9.0	10.4

was calculated using the formula  $d_{\text{pore}}(\text{BET}) = 4000 \times V_{\text{tot}}/A_{\text{BET}}$ .

The structures and microstructures of the samples were studied via high-resolution transmission electron microscopy (HRTEM) on a JEM 2010 electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV and a limiting lattice resolution of 0.14 nm. The images were recorded on a CCD matrix Soft Imaging System (Germany). The electron microscope was equipped with an XFlash energy dispersive spectrometer of X-ray characteristic radiation (EDX) (Bruker, Germany) with a semiconductor Si detector with an energy resolution of 130 eV.

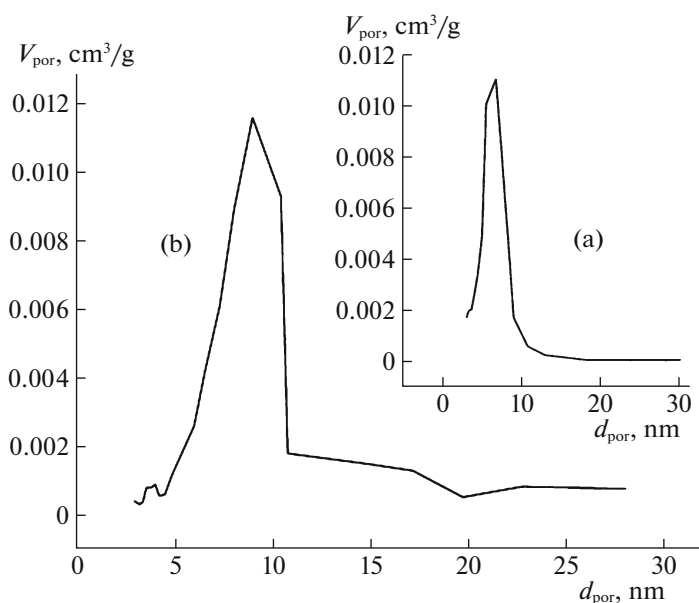
The chromatographic parameters were measured on a Kristall 2000 chromatograph equipped with a thermal conductivity detector (TCD). Helium was used as the carrier gas (30 cm<sup>3</sup>/min). The temperature of the column oven was maintained with an accuracy of  $\pm 0.5^\circ\text{C}$ . The chromatographic data were processed with the NetChrom software.

Model mixtures with a given concentration based on argon were prepared in metal cylinders (10 L) using manometric volumetry to perform each experiment. A mixture of constant ( $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ ) and  $\text{C}_1\text{--C}_2$  hydrocarbon gases was prepared in cylinder 1, and a mixture of  $\text{C}_3\text{--C}_4$  hydrocarbon gases (10 vol % each) was in cylinder 2. Liquid saturated and unsaturated  $\text{C}_5\text{--C}_8$  hydrocarbons were mixed in separate chromatography vials with no specific concentration of components.

A model mixtures of constant and hydrocarbon gases from the gas cylinders and liquid saturated and unsaturated hydrocarbons were sampled from a chromatography vial with a syringe and injected into the chromatograph.

## RESULTS AND DISCUSSION

Table 2 shows the textural properties of the adsorbents obtained from  $\gamma\text{-Al}_2\text{O}_3 + 10 \text{ wt } \% \text{ PI-1B}$ .



**Fig. 2.** Pore distribution determined from nitrogen desorption for (a)  $\gamma\text{-Al}_2\text{O}_3$  without HCl treatment + 10 wt % PI-1B; (b)  $\gamma\text{-Al}_2\text{O}_3$  after HCl treatment + 10 wt % PI-1B; and (c) samples aged thermally at  $T_{\text{ag}} = 450^\circ\text{C}$ .

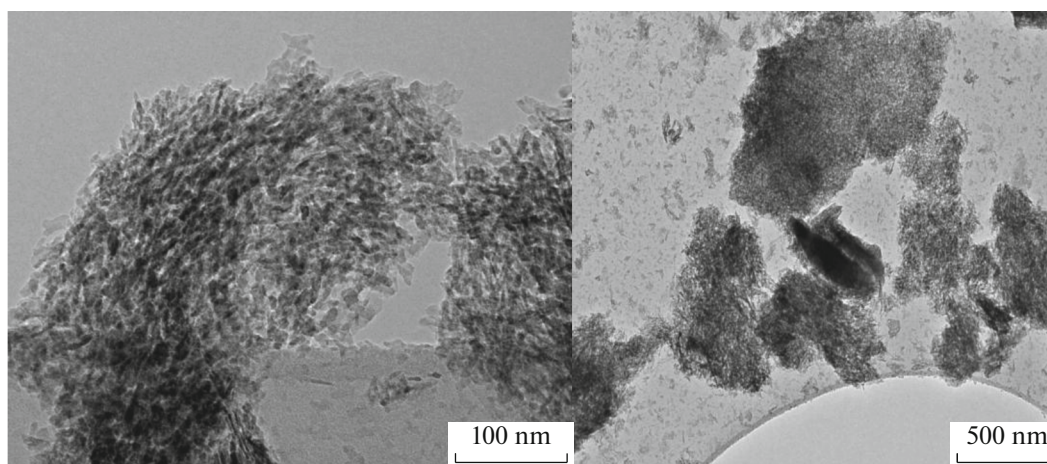


Fig. 3. HRTEM micrographs of  $\gamma\text{-Al}_2\text{O}_3$  after HCl treatment + 10 wt % PI-1B with the size of particles ( $T_{\text{ag}} = 450^\circ\text{C}$ ).

The root-mean-square deviation (RMSD) was 5% when measuring the specific surface and 10% of the volume and diameter of pores.

Analysis of the nitrogen desorption curves showed that the removal of active sites, the subsequent modification of 10 wt % PI-1B aluminum oxide, and its thermal aging at  $450^\circ\text{C}$  produced a more uniform surface of  $190.4\text{ m}^2/\text{g}$ . The average pore diameter was 10.4 nm, and there were no micropores (Table 2). It should be noted that the pore diameter varied from 5 to 11 nm (Fig. 2b), while it was 1–13 nm for an adsorbent with an untreated initial surface. The average diameter of the pores was 6–7 nm (Fig. 2a).

Figure 2 shows the pore distribution curves determined from nitrogen desorption for  $\gamma\text{-Al}_2\text{O}_3$  + 10 wt % PI-1B without and after treating the initial support with hydrochloric acid.

Samples for electron microscopy were deposited onto perforated carbon-coated copper or molybdenum grids. To achieve a uniform distribution of particles, the samples were ultrasonicated in ethanol using an UZD-1UCH2 disperser. The obtained suspension was uniformly dropped on the grid and dried in air.

HRTEM data indicate that each sample consisted of  $\gamma\text{-Al}_2\text{O}_3$  particles coated with layers of amorphized

carbon. The size of particles varied from 10 nm (single crystallites) to several microns (Fig. 3).

Higher magnifications showed that the surfaces of  $\gamma\text{-Al}_2\text{O}_3$  particles were covered with layers of amorphized carbon (Fig. 4). The thickness of the layers varied from a monolayer to several layers. In addition, HRTEM images revealed the porous structure of the sample, in which the size of pores also varied from 1 to 10 nm. The pores were also covered with a layer of amorphous carbon.

EDX data indicate (Table 3) that carbon was distributed uniformly, predominantly on surface layers. However, there were areas with relatively low amounts of carbon.

The HRTEM data are in good agreement with the texture properties for  $\gamma\text{-Al}_2\text{O}_3$  after HCl treatment + 10 wt % PI-1B, which was thermally treated at  $T_{\text{ag}} = 450^\circ\text{C}$ . They also confirm our assumption about the formation of a homogeneous surface on this adsorbent.

Chromatographic properties were studied in analyzing a model mixture (Table 4) on  $\gamma\text{-Al}_2\text{O}_3$  + 10 wt % PI-1B, and were compared to earlier data for  $\gamma\text{-Al}_2\text{O}_3$  + 10 wt % PAA with subsequent imidization in PI-1B.

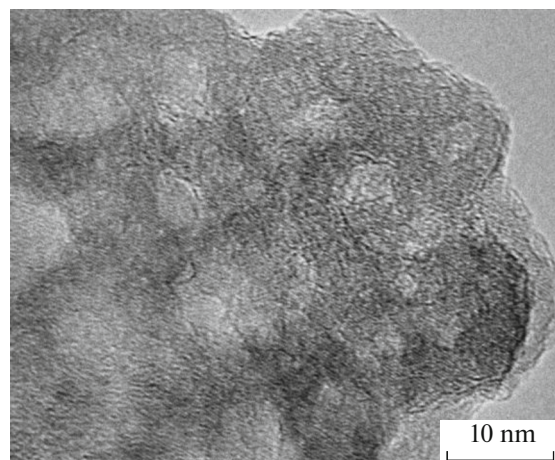
Aluminum oxide modification with polyamic acid and subsequent high-temperature imidization were studied in [8]. The surface of the obtained material was sufficiently developed ( $200.1\text{ m}^2/\text{g}$ ) to satisfactorily separate permanent gases and light hydrocarbons. The peak of carbon dioxide was quite wide, however, due to the surface heterogeneity and the formation of pores with narrower diameters of 6–7 nm (Table 2).

It was shown [11] that impregnating a diatomite support with a polyimide solution is most convenient, since polyimide is a more stable compound than PAA, which is subject to hydrolysis.

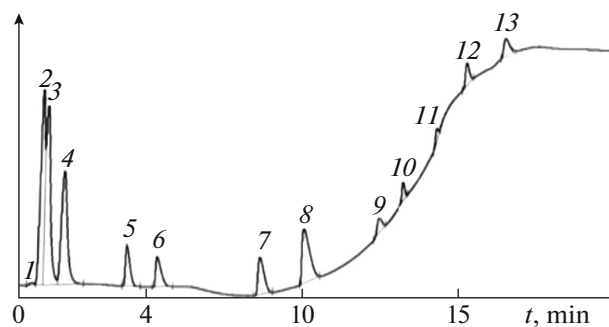
The  $\gamma\text{-Al}_2\text{O}_3$  without HCl treatment sample was therefore impregnated with a polyimide solution at the next stage. Table 2 shows that the surface and the volume of

Table 3. Zones of surface analysis and elemental composition of  $\gamma\text{-Al}_2\text{O}_3$  after HCl treatment + 10 wt % PI-1B

Zones of analysis	C	Al	Si	Cl
1	24.39	73.38	0.49	1.73
2	28.68	71.07	0.06	0.19
3	24.00	75.38	0.06	0.56
4	5.02	94.56	0.09	0.33



**Fig. 4.** HRTEM micrographs of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after HCl treatment + 10 wt % PI-1B with the size of pores ( $T_{ag} = 450^\circ\text{C}$ ).



**Fig. 5.** Separation chromatogram of permanent gases, CO<sub>2</sub>, and C<sub>1</sub>–C<sub>8</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> without HCl treatment + 10% PI-1B at  $T_{ag} = 250^\circ\text{C}$ . Chromatographic conditions:  $T = 30^\circ\text{C}$  for 2 min and then programmed heating at a rate of 10 K/min to 230°C. (1) Hydrogen, (2) nitrogen + oxygen, (3) CO, (4) methane, (5) ethane + CO<sub>2</sub>, (6) ethylene, (7) propane, (8) propylene + acetylene, (9) butane, (10) pentane, (11) hexane, (12) heptane, and (13) octane.

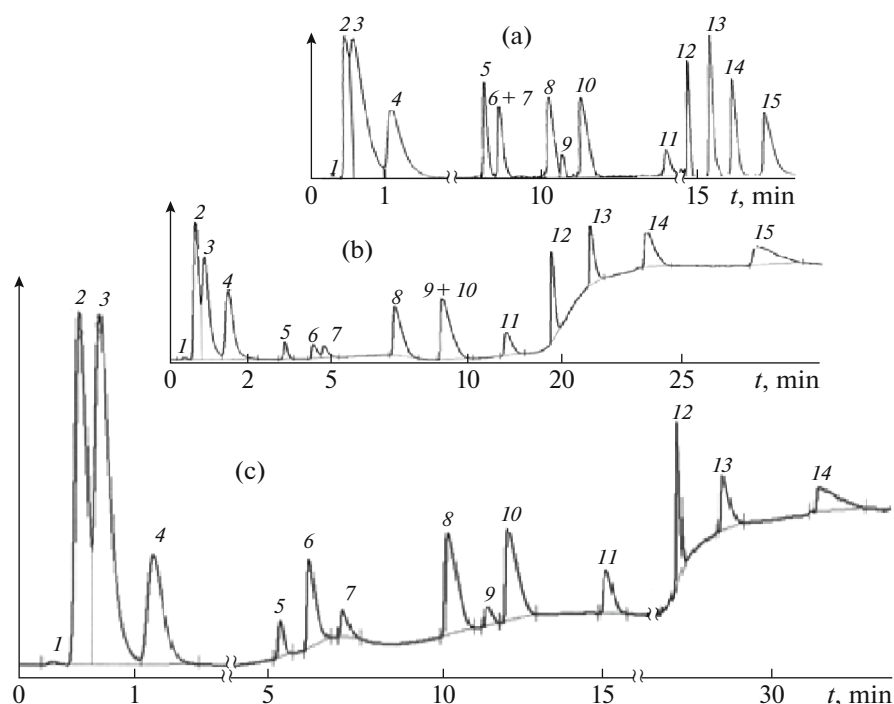
pores considerably decreased after thermal aging at 250°C, while the diameter of pores remained virtually unchanged. Data from a chromatographic analysis of the model mixture showed that carbon dioxide was eluted together with ethane and acetylene with propylene (Fig. 5).

The adsorption properties of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> without HCl treatment + 10 wt % PI-1B adsorbent remained unchanged (Table 2) upon raising the temperature ( $T_{ag} = 450^\circ\text{C}$ ). The order of release of the components of the analyzed mixture remained the same, though the retention times grew (Table 4).

**Table 4.** Physicochemical properties and retention times of components of a model mixture

Sorbate	$M$	$T_b, ^\circ\text{C}$	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> without HCl treatment + 10 wt % PAA [8]		$\gamma$ -Al <sub>2</sub> O <sub>3</sub> without HCl treatment + 10 wt % PI-1B		$\gamma$ -Al <sub>2</sub> O <sub>3</sub> after HCl treatment + 10 wt % PI-1B				
			$T_{ag}, ^\circ\text{C}$						250	350	450
			250	450	250	450	250	350			
H <sub>2</sub>	2	−252.7	0.81	0.52	0.65	0.70	0.74	0.58	0.65		
O <sub>2</sub>	32	−182.9	0.93	0.60	0.75	0.82	0.83	0.67	0.77		
N <sub>2</sub>	24	−210	0.93	0.60	0.75	0.82	0.83	0.67	0.77		
CO	28	−192	1.02	0.65	0.81	0.91	0.92	0.74	0.86		
CO <sub>2</sub>	44	−78.6 (0.52 MPa)	5.09	5.62	3.52	10.36	4.28	4.20	6.10		
CH <sub>4</sub>	16	−161.6	1.12	2.71	0.99	1.07	1.13	0.88	1.12		
C <sub>2</sub> H <sub>2</sub>	26	−83.8	14.10	11.05	9.79	11.16	9.04	9.31	11.55		
C <sub>2</sub> H <sub>4</sub>	28	−103.7	5.14	8.66	4.58	5.45	4.28	4.62	7.11		
C <sub>2</sub> H <sub>6</sub>	30	−88.6	3.41	6.62	3.52	3.99	3.61	3.12	5.19		
C <sub>3</sub> H <sub>6</sub>	42	−47.8	12.66	15.82	9.79	10.36	9.98	9.31	12.19		
C <sub>3</sub> H <sub>8</sub>	44	−42.1	8.83	9.78	8.23	8.51	8.51	7.43	10.35		
C <sub>4</sub> H <sub>10</sub>	58	−0.5	15.92	12.95	12.46	12.80	13.62	11.83	15.16		
C <sub>5</sub> H <sub>12</sub>	72	36.1	21.78	16.70	12.52	16.13	14.12	14.94	17.76		
C <sub>6</sub> H <sub>14</sub>	86	68.7	27.33	20.20	14.35	19.74	16.83	17.99	24.00		
C <sub>7</sub> H <sub>16</sub>	100	98.4	32.35	23.83	16.07	26.50	19.49	22.38	37.53		
C <sub>8</sub> H <sub>18</sub>	114	125.7	36.77	26.48	18.24	40.25	23.70	30.96	—		

Chromatographic conditions:  $T = 30^\circ\text{C}$  for 2 min and a heating rate of 10 K/min up to 230°C.



**Fig. 6.** Chromatogram showing separation of permanent gases,  $\text{CO}_2$ , and C1–C8 on  $\gamma\text{-Al}_2\text{O}_3$  after HCl treatment + 10% PI-1B at  $T_{\text{ag}}$ : (a) 250, (b) 350, and (c) 450°C. Chromatographic conditions:  $T = 30^\circ\text{C}$  for 2 min and then programmed heating at a rate of 10 K/min to 230°C. (1) Hydrogen, (2) nitrogen + oxygen, (3) CO, (4) methane, (5) ethane, (6)  $\text{CO}_2$ , (7) ethylene, (8) propane, (9) acetylene, (10) propylene, (11) butane, (12) pentane, (13) hexane, (14) heptane, and (15) octane.

We then studied the properties of  $\gamma\text{-Al}_2\text{O}_3$  from whose initial surface active centers (iron, sodium, and titanium) were removed earlier and whose absence was confirmed by EDX data (Table 3). Aluminum oxide was mixed with concentrated hydrochloric acid and held for 30 min. It was then washed with distilled water until it was neutral, dried to a constant weight, and modified with polyimide synthesized according to the second technique.

Table 2 shows that preliminary treatment of the initial aluminum oxide had a weak effect on its surface and the volume of pores, but their diameter grew to 7.8 nm for  $\gamma\text{-Al}_2\text{O}_3$  without HCl treatment and 9.0 nm for  $\gamma\text{-Al}_2\text{O}_3$  after HCl treatment.

The surface of  $\gamma\text{-Al}_2\text{O}_3$  after HCl treatment + 10 wt % polyimide considerably decreased, from 228.9 to 190.4  $\text{m}^2/\text{g}$  upon raising temperature of thermal aging to 450°C, and the diameter of pores was increased from 9.0 to 10.4 nm (Table 2).

Changes in textural properties of the adsorbent had a considerable effect on its chromatographic properties. Figure 6 shows the behavior of sorbates during elution from the surface of a test material. The sample aged thermally at  $T_{\text{ag}} = 250^\circ\text{C}$  (Fig. 6a) was able to separation of constant gases, acetylene eluted between propane and propylene, and carbon dioxide appeared as one peak with ethylene.

Carbon dioxide eluted with a separate peak and came out between ethane and ethylene upon raising the temperature of thermal aging to 350°C (Fig. 6b), while acetylene did not separate with propylene. Hydrogen was separated, but nitrogen and oxygen were only half separated from carbon monoxide.

Raising the temperature of thermal aging to 450°C reduced the surface and increased the diameter of the pores (Table 2). The number of micropores decreased during calcination, and pores of the same diameter predominated ( $\approx 10.4$  nm).

Our results (Table 2 and Fig. 6c) testify to the creation of a  $\gamma\text{-Al}_2\text{O}_3$  after HCl treatment + 10 wt % of polyimide adsorbent, whose separation capacity for any pair of components was higher than 1, with the exception of CO and nitrogen + oxygen, for which the resolution was  $\approx 0.5$ . It should be noted that the symmetric peak of carbon dioxide was separated from ethane and ethylene, while that of acetylene was between propane and propylene.

## CONCLUSIONS

Preliminary removal of active sites from the surface of aluminum oxide, modification with polyimide, and subsequent thermal aging at 450°C contributed to the creation of a promising chromatographic adsorbent (selective layer) with adjustable pores 10.4 nm in

diameter for separating permanent gases and mixtures of them with C<sub>1</sub>–C<sub>8</sub> hydrocarbons.

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