



Determination of Sorption Capacity for Different Sorbates of Adsorbents Used for Dearomatization and Deparaffinization of Motor Oils

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Abstract: The sorption capacity of the selected adsorbents was determined - silica gel CSL (coarse-pored silica gel lump) and synthetic zeolite CaA according to the standards of aromatic and n-paraffin hydrocarbons using the cryoscopic method. The amount of adsorbed substance in weight percent for each portion of the filtrate is converted into grams, summed up and referred to 100 g of the adsorbent. After that, the silica gel was washed with distilled water until the reaction to the Cl⁻ ion was negative, unloaded onto filtered paper, and left to dry in the open air. The solution was passed in a chromatographic column through an adsorbent. The amount of adsorbed substance A was calculated. Type A synthetic zeolites include zeolites with radii: KA (0,3 nm), NaA (0,4 nm) and CaA (0,49 nm). CaA zeolite adsorbs hydrocarbons and alcohols of normal structure only (regardless of the chain length) due to the size of the input window corresponding to the size of their critical diameters. The synthesized zeolites are powders and in order to use them under dynamic conditions, they are granulated with the addition of a binder, usually natural clays, and molded into tablets, cylinders, or balls. The sorption capacity of the synthetic zeolite CaA for n-hexane from the liquid phase under dynamic conditions is given. As can be seen from the given data, benzene is practically not adsorbed by CaA zeolite, but is adsorbed by silica gel. Moreover, CSL silica gel activated with hydrochloric acid has a higher capacity.

Keywords: Aromatic Hydrocarbons, n-paraffin Hydrocarbons, n-hexane, Benzene, Cyclohexane, Adsorbent, Silica GEL, Brigleb-Stuart Models

1. Introduction

In the modern gas, chemical and oil refining industries, the adsorption method, as the simplest and most convenient, is widely used for deep purification and drying of process streams, improving the quality of raw materials and various products, as well as separating and separating various complex technical mixtures. The purpose of this work is to determine the sorption capacity of adsorbents used to improve the quality of light oil products in the processes of dearomatization and denormalization, since modern petroleum feedstocks are highly paraffinic and highly viscous, as well as products derived from them. In addition, in order for oil products to meet European standards, it is necessary to reduce the amount of aromatic hydrocarbons.

The sorption capacity of the selected adsorbents was determined - silica gel CSL (initial and activated with hydrochloric acid) and synthetic zeolite CaA according to the standards of aromatic and n-paraffin hydrocarbons: benzene and n-hexane in the liquid phase under dynamic conditions by the cryoscopic method [1].

The essence of determining the selectivity and dynamic capacity of adsorbents by the cryoscopic method is to change the concentration of the reference solution chromatographed through the adsorbent and is determined according to the change in the depression of the crystallization temperature of the solution.

2. Methods

The analysis is carried out as follows: two percent standard solution of organic matter in cyclohexane is passed in a glass column through 10 g of the adsorbent (0,25-0,50 mm, previously dehydrated) until it is completely saturated, i.e. when the crystallization temperature of the filtrate (t_3) does not become equal to the crystallization temperature of the initial reference solution (t_2). Since the crystallization temperature of the initial cyclohexane (t_1) and reference solution (t_2) is determined in advance, the entire analysis is reduced to determining the crystallization temperature of the filtrate (t_3). The filtrate is taken by volume in portions of 12,85 ml (corresponding to 10 g). In each portion, the crystallization temperature (t_3) is determined, and then the amount of adsorbed substance (mol.%) is calculated using the formula:

$$A = \frac{t_3 - t_2}{t_1 - t_2} \cdot 100\% \quad (1)$$

The mole percentages of the adsorbed substance can be recalculated in weight percent using the formula:

$$P = \frac{A/100 \cdot M}{(1-A/100) \cdot 84,16 + A/100 \cdot M} \cdot 10 \quad (2)$$

where M is molecular mass of a substance; 84,16 – molecular mass of cyclohexane.

The amount of adsorbed substance in weight percent for each portion of the filtrate is converted into grams, summed

up and referred to 100 g of the adsorbent.

To increase the sorption capacity of silica gel, it was activated by a special method.

To activate the CSL silica gel, concentrated (35%) hydrochloric acid was used. Hydrochloric acid was poured into a porcelain cup with silica gel (0,25-0,50 mm) and periodically stirred for 4 hours.

After that, the silica gel was washed with distilled water until the reaction to the Cl⁻ ion was negative, unloaded onto filtered paper, and left to dry in the open air.

3. Result

The analysis was carried out in the specified sequences: 10 g of activated silica gel was weighed CSL 0,25-0,50 mm and dried in an oven for 6 hours at a temperature of 180°C. A 2% standard solution of benzene in cyclohexane was prepared and the crystallization temperature (t_2) was determined. The solution was passed in a chromatographic column through an adsorbent. The filtrate was taken by volume in portions of 12,85 ml (corresponding to 10 g). In each portion, the crystallization temperature (t_3) was determined, and then the amount of adsorbed substance A (mol.%) was calculated, then the mole percentages of the adsorbed substance were recalculated into weight percent P, wt. by formulas (1) and (2). Table 1 shows the data on the determination of the dynamic capacity of the original and activated silica gel CSL for benzene.

Table 1. Dynamic capacity of the initial and activated silica gel CSL for benzene (silica gel batch 262, R_{por} 7 nm).

Model Blend	№ filtrate samples	Crystallization temperature, °C	Adsorbed as a percentage of the substance in solution		Dynamic capacity, %			
			mole. %, A	mass., %, P	g/10	g/100	до проскока	полная
<i>Silica gel initial</i>								
2% solution in cyclohexane	1	4,61	53,86	51,97	0,102	1,02		
	2	3,40	22,68	21,37	0,043	0,43		1,45
	3	2,52	0	0	0	0	0	
<i>Silica gel activated</i>								
$t_1 = 6,40^\circ\text{C}$	1	6,40	100,0	100,0	0,200	2,00	2,00	
$t_2 = 2,52^\circ\text{C}$	2	3,65	29,12	27,58	0,055	0,55	0,55	2,55
	3	2,52	0	0	0	0		

Since the change in t_2 is proportional to the concentration of the solution, then, using the experimentally found values of t_3 , it is possible to build "output curves", plotting the total amount of collected filtrate along the abscissa axis, and t_2 along the ordinate axis (Table 1). In this case, the area of the figure ABED corresponds to the full dynamic capacity of the sorbent, and the area of the rectangle ABEF corresponds to its dynamic capacity to breakthrough, on the basis of which the working capacity of the adsorbent is calculated. By the area ABEF (S_1) and ABSD (S_0) it is possible to graphically determine the capacity of the adsorbent.

$$\frac{m_1}{m_0} = \frac{S_1}{S_0}, m_1 = m_0 \frac{S_1}{S_0} \quad (3)$$

where m_0 is the amount of substance injected.

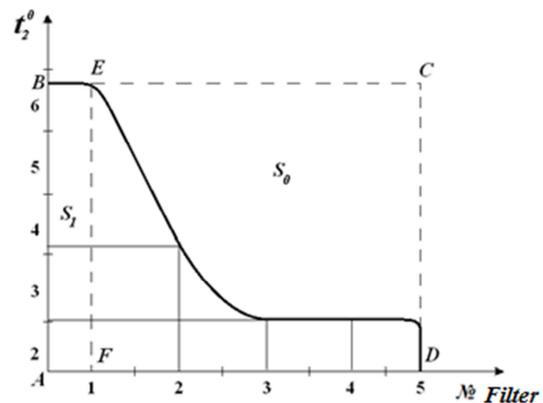


Figure 1. The output curve of the dynamic capacity of the CSL sorbent for benzene.

The structure of type A zeolites consists of large and small adsorption cavities. The chemical formula of Zeolite is $\text{CaA}:\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 4,5\text{H}_2\text{O}$. The elementary cell of the sorbent includes one large and one small cavity. The cavity has an almost spherical shape with a diameter of 1,14 nm. It is connected to six adjacent large cavities by eight-membered oxygen rings 0,42 nm in diameter and to eight small cavities by six-membered oxygen rings 0,22 nm in diameter. The volume of the large cavity is $V_b = 77,6 \text{ nm}^3$. The small cavity is also spherical, its diameter is 0,66 nm, volume $V_s = 15 \text{ nm}^3$ [2] (Figure 2).

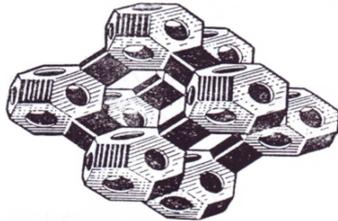


Figure 2. Structure of synthetic type A zeolites.

4. Discussion

Type A synthetic zeolites include zeolites with radii: KA (0,3 nm), NaA (0,4 nm) and CaA (0,49 nm). CaA zeolite adsorbs hydrocarbons and alcohols of normal structure only (regardless of the chain length) due to the size of the input window corresponding to the size of their critical diameters (Table 2), and therefore it is widely used in the process of

separating multicomponent organic substances on a molecular sieve basis.

The critical diameters (d_c) and lengths (L_{mol}) of n-paraffin hydrocarbon molecules, determined by the Brigleb-Stuart models, are as follows [3, 4]:

Table 2. The critical diameters (d_c) and lengths (L_{mol}) of n-paraffin hydrocarbon molecules.

Substance	L_{mol} , nm	d_c , nm
n-Hexane	1,05	0,47
n-heptane	1,18	0,47
n-octane	1,30	0,47
n-nonan	1,43	0,47
n-decan	1,55	0,47
n-undecan	1,68	0,47

From the table above, it can be understood that the critical diameter of all n-alkanes is 0,47 nm, the increase in the length of the molecules of n-paraffin hydrocarbons is ~ 0,12-0,13 nm. Based on the critical diameter of n-alkanes, it can be said that they will all be adsorbed by CaA zeolite, since they are commensurate with the size of the CaA zeolite inlet channel – 0,49 nm (5 Å) and it clear that CaA zeolite does not adsorb other substances [5-15].

The synthesized zeolites are powders and in order to use them under dynamic conditions, they are granulated with the addition of a binder, usually natural clays, and molded into tablets, cylinders, or balls. The sorption capacity of the synthetic zeolite CaA for n-hexane from the liquid phase under dynamic conditions is given in Table 3.

Table 3. Dynamic capacity of CaA zeolite for n-hexane.

Model mix	№ samples filtrate	Crystallization temperature, °C	Adsorbed as a percentage of the substance in solution		Dynamic capacity, %			
			mole. %, A	mass., %, P	g/10	g/100	before the slip full	
2% solution in cyclohexane $t_1 = 6,40^\circ\text{C}$ $t_2 = 2,40^\circ\text{C}$	1	6,40	100,0	100,0	0,200	2,00	4,00	7,11
	2	6,40	100,0	100,0	0,200	2,00		
	3	5,50	77,50	77,87	0,155	1,55		
	4	3,90	37,50	38,00	0,076	0,76		
	5	3,00	15,00	15,27	0,030	0,30		
	6	2,70	7,500	7,651	0,015	0,15		
	7	2,70	7,500	7,651	0,015	0,15		
	8	2,70	7,500	7,651	0,015	0,15		
	9	2,50	2,500	2,553	0,005	0,05		
	10	2,40	0	0	0	0		

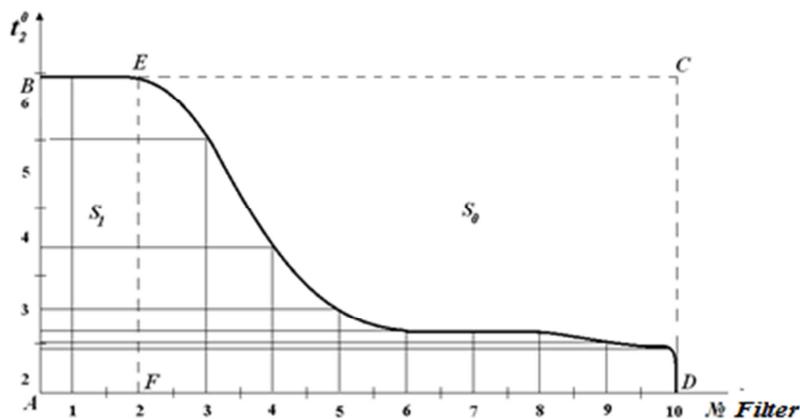


Figure 3. The output curve of the dynamic capacity of the CaA sorbent for n-hexane.

5. Conclusion

As can be seen from the given data, benzene is practically not adsorbed by CaA zeolite, but is adsorbed by silica gel. Moreover, CSL silica gel activated with hydrochloric acid has a higher capacity than the original 2,55 compared to 1,45% and is completely inert to n-hexane. Therefore, activated silica gel should be used in dearomatization processes, and synthetic zeolite CaA should be used for denormalization.

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