

Toluene Adsorption on Polyhydroxyaluminum Montmorillonite

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Abstract:

Changes in the surface properties and porous structure of montmorillonite were studied when sodium ions were replaced by polyhydroxyaluminum ones. A preliminary thermal vacuum has a significant effect on the adsorption properties of polyhydroxyaluminum montmorillonite. According to the series of isotherms of sorption of toluene on dehydrated polyhydroxyaluminium montmorillonites, the dependence of the temperature changes of PHAM (293K - 423K - 523K - 773K) on the amount of adsorption and desorption of toluene was established. The appearance of maxima is due to the interaction of adsorbate molecules with active centers and with each other due to compaction during filling of the volumes of slit micropores.

Introduction

An increasingly wide use of natural sorbents the need to study the nature of the surface and porous structure of these adsorbents [1]. A large interest to such intercalates and, in particular, to montmorillonites clays results from their high thermal stability and zeolite like structure [2-6]; they can be used as adsorbents, carriers for the gas chromatography, fillers for various plastics and paints, as well as for deactivation of toxic substances.

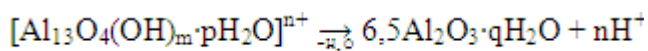
In this work, we studied the adsorption of toluene vapors on polyhydroxyaluminum montmorillonite (PHAM) samples treated at temperatures low and above the temperature of the transformation of hydroxycations in aluminum oxide clusters.

One of the ways to create a microporous structure of layered clay minerals with an expanding structure is to replace exchangeable ions with polyhydroxyaluminum ones. The study of the adsorption of molecules of different structures on polyhydroxyaluminum microporous adsorbents will make it possible to elucidate the role of the microporous structure and modifying cations in the adsorption interaction. The accumulation of experimental data on polyhydroxyaluminum microporous adsorbents is of great importance due to the fact that they have a high adsorption capacity and are suitable in adsorption technologies, especially in processes proceeding at high temperatures. The preparation conditions and adsorption properties of montmorillonite adsorbents with modifying polyhydroxyaluminum cations (PHAK) are described in [7-16]. It was found that different PHAK, when introduced into exchange positions of montmorillonite, move the layers apart along the c axis, resulting in the formation of slit-shaped micropores. Taking into account the fact that the dehydration of intercalated clays under certain conditions is accompanied by the transfer of PHAK into alumina clusters [2, 17], in this work we studied the adsorption of toluene vapor on samples of polyhydroxyaluminum montmorillonite (PHAM).

Experimental

The object for the study was Na-montmorillonite (NaM) (Navbahor deposit, Uzbekistan) with the following chemical composition (wt%); SiO₂-57,91%, TiO₂-0,35, Al₂O₃-13,69, Fe₂O₃-5,10, MgO-1,84, CaO-0,48, Na₂O-1,53, K₂O-1,75, P₂O₅-0,43, SO₃-0,75 [7].

Samples were modified by treating a 3 % suspension of montmorillonite clay with an aluminum hydrochloride solution at a molar ratio OH/Al=2,37. A solution with such basicity gives rise to the formation of a complex containing seven-charged PHACs $[Al_{13}O_4(OH)_{12}(H_2O)_{24}]^{7+}$. An exothermal effect observed in a PHAM thermogram at 600 K indicates the transformation of PHACs located at exchange sites of the mineral in aluminum oxide clusters, $Al_2O_3 \cdot qH_2O$ [5].



Water removal upon heating to 750-800K does not change noticeably the interplanar spacing of PHAM. According to the X-ray diffraction data, the spacing ($\Delta d_{001}=0,875$ nm) between neighbor basal planes of PHAM along the *c* axis decreases by 20% after heating the samples at 773K. The silt-like micropores are accessible for toluene molecules with a diameter of 0,67 nm.

The isotherms of toluene vapor adsorption were measured with a Mac-Bain balance. Before adsorption measurements, PHAM samples were dried in vacuum at 293, 423, 523 or 773K (samples I-IV, respectively) and the NaM sample-at 423K (sample V) to a residual pressure in the system of about $1,33 \cdot 10^{-3}$ Pa.

The isotherms of toluene adsorption on NaM and PHAM are presented in Fig. 1. Adsorption of toluene and benzene on NaM is governed mainly by the surface properties of this clay mineral. At moderate and high relative pressures P/P_s , when multilayers are formed and the capillary condensation of toluene proceeds in pores formed by the lamellar mineral particles the hysteresis loops are observed on isotherms. The loop widths for the isotherms measured for NaM and PHAM samples are approximately equal. Adsorption isotherms measured for PHAM samples at low toluene pressures steeply rise that is typical of PHAM treated at microporous adsorbents. According to [8], the structure of PHAM treated of 423K remains intact and has the highest sorption capacity.

Most of the physically sorbed moisture is removed upon the PHAM evacuation at room temperature (293 K), and the initial adsorption of toluene (at low P/P_a) markedly increased compared to the adsorption on NaM. Being heated in a vacuum at 293-423 K, PHAM becomes almost entirely dehydrated, therefore, sample II demonstrated the highest adsorption value. The thermal treatment at 423-523 K only slightly decreases the adsorption capacity of PHAM. After the treatment of 523-773 K, toluene adsorption on sample IV noticeably decreases because of the transformation on PHACs in aluminum oxide clusters. Initial parts of isotherms 1-5 (Fig. 1.) at $P/P_s \leq 0,20-0,24$ are reversible. The pattern of hysteresis loops observed for toluene adsorption/desorption on sample I-V may be attributed to the B-type, according to the de Boer classification [9, 16]. Hysteresis of this type is typical of the adsorption in open slit-like pores. Relatively sharp inflections on the adsorption isotherms at $P/P_s \geq 0,2-0,3$ are related to the disordering of the thixotropic structure [17] formed upon the saturation of sorbents.

Because of a dramatic change in the free sorption volume upon the modification of montmorillonite clay, at low and moderate P/P_s , the values of toluene adsorption on PHAM samples are 4-6 fold higher than those on the original mineral (NaM). Using the adsorption isotherms of toluene, we calculated the sorption volumes of thermotreated PHAM and NaM samples at $P/P_s=0,2$ (W), 0,4 (W_o) and 1,0 (V_s), as well as the mesopore volume $W_{meso}=V_s-W_o$. Corresponding data are listed in the table. It is seen that when the temperature of the pretreatment of PHAM increases from 293 to 423 K, W_o and V_s increase by 12 and 20 %, respectively, and reach their maximal values. Further, within a range of 423-523 K, W_o and V_s values decrease by 6 and 8 %, respectively. As was mentioned above, the transformation of PHACs in aluminum oxide clusters at $T > 600K$ is accompanied by the reduction in micropore volume W_o and the sorption volume at the saturation V_s . Indeed, the sorption volumes W_o and V_s of sample IV are smaller by 29 and 25 %, respectively, than

those of sample II. The adsorption of toluene vapors at $P/P_s > 0,4$ results mainly in filling the volume of mesopores. This volume amounts to 28 and approximately 35 % of the total pore volume for sample I and samples II-IV, respectively.

A comparison of the sorption volumes of the thermally treated PHAM samples demonstrates that W_o and V_s values for toluene are somewhat larger than those for benzene[18]. For example, these differences are 9 and 24 % for sample 1 and 7 and 30 %, for samples II and III, respectively; while the sorption volumes of sample IV concerning both adsorbates are similar. It is obvious that the steric factor cannot be the main reason for the observed differences, because the sorption volume with respect to benzene must be larger than for toluene since the molecular size of toluene is noticeably larger than that of benzene. Seemingly, a larger pore volume of PHAM dehydrated at 293-523 K with respect to toluene is mainly explained by a partial "opening" of additional volumes during its sorption. If so, PHAM is deformed to a much higher extent under the effect of adsorption in its mesopores than during the micropore filling.

The effect of dehydration conditions on the adsorption properties of PHAM was studied. It was shown that, despite the change in the nature of the supporting polyhydroxyaluminum cations resulted from the dehydration of the modified clay, its structure remains, as a whole, microporous.

Table. Sorption volumes ($\text{m}^3 \text{kg}^{-1}$) of montmorillonite samples with respect to toluene

Sample no	Dehydration temperature K	$W \cdot 10^3$	$W_o \cdot 10^3$	$V_s \cdot 10^3$	$W_{\text{mes}} \cdot 10^3$
Polyhydroxyaluminum montmorillonite					
I	293	0,106	0,119	0,187	0,048
II	423	0,121	0,135	0,208	0,073
III	523	0,118	0,127	0,191	0,064
IV	773	0,087	0,096	0,155	0,059
Na-montmorillonite					
V	423	0,022	-	0,092	-

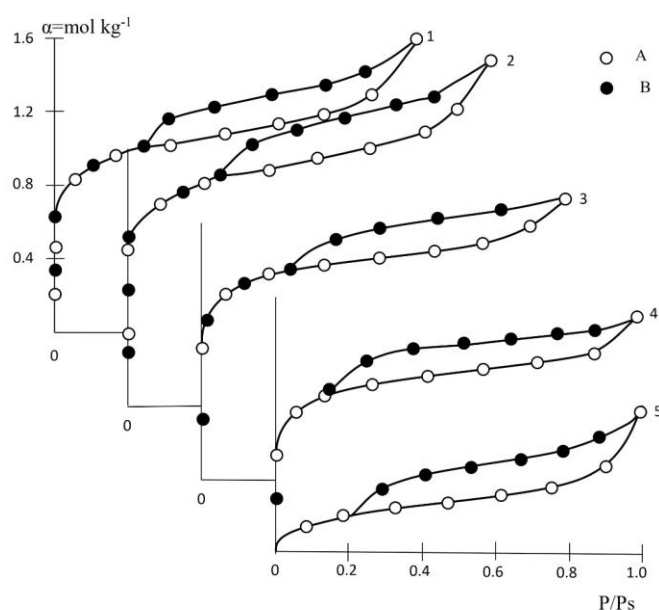


Fig. 1. Adsorption and desorption isotherms of toluene on PHAM samples treated at (1) 293, (2) 423, (3) 523 and (4) 773 K and on (5) NaM. (A) Adsorption and (B) desorption. Isotherms (1-4) are shifted by 0.4 mol kg^{-1} and 0.1 along the a and P/P_s axes, respectively.

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