# ADSORPTION AND THERMODYNAMIC STUDY OF PYROGENIC ALUMINA PROPERTIES

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## Abstract

Adsorption of *n*-pentane, triethylamine, diethyl ether, acetonitrile and chloroform has been investigated on pyrogenic alumina ($S$=140 m$^2$ g$^{-1}$). The results of our studies have shown the presence of active sites on the surface of pyrogenic alumina with irreversible adsorption of electron-donating molecules and CHCl$_3$ and the dependence of energetic surface properties on electronic structure of adsorbate, quantity of adsorbed substance and hydration degree of the surface. On the hydrated oxide surface the water molecules screen the active sites of the surface, which resulted in changing of interaction energy of adsorbent-adsorbate and decreasing the region of irreversible adsorption of organic bases and CH-acid.

**Keywords:** adsorption, adsorption heats, pyrogenic alumina, surface sites

## Introduction

The study of adsorption energy directly gives qualitative and quantitative characteristics of the adsorption interaction nature. Among static methods of adsorbent properties investigation, the method consisting in the weighing of an adsorbent together with an adsorbed substance is more frequently used. The isotherms of adsorption i.e. the number of following equilibrium pressures, which are in accordance with a quantity of adsorbed substance, carry some information on the surface properties of solids. The presence of a single isotherm for an adsorption–desorption process allows to define the main characteristics of adsorbents such as surface area value and porosity (values of radius and volume of pores taking part in adsorption process). During adsorption investigations the reliability of experimental data are determined by the measurement accuracy of pressure ($P$), the quantity of adsorbed substance ($a$) and temperature ($T$).

The presence of isotherms, measured under different temperatures permits to contract isosters i.e. dependencies ln$P$ on $1/T$, which are straight-line and calculate isosteric adsorption heats from their slopes.

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## Experimental

The pyrogenic aluminium oxide, an amorphous non-porous material with small inclusions of crystalline phase $\gamma$-$Al_2O_3$ and a surface area 140 m$^2$ g$^{-1}$ was chosen as an object for investigation. Adsorption studies have been carried out on a precision vacuum experimental set-up, described in [1].

The choice of molecules-sounds for basic-acidic properties investigations is the matter of importance. Molecules of triethylamine (TEA), diethyl ether (DE) and acetonitrile (AN) were used for studying acidic properties of $Al_2O_3$ because their electron-donating properties have significant differ allowing to define the acidic sites with different strength taking part in adsorption process. These molecules can be used to study both Brønsted and Lewis acidic sites. Molecules of a week base – chloroform – were used to estimate the proton-donating properties due to their ability to form H-complexes and do not interact with protonic and Lewis sites on the surface of solid [2]. The adsorption properties of alumina relative $n$-pentane, where adsorption interaction takes place at the expense of dispersion forces, were also studied for comparison with molecules mentioned before.

The samples for adsorption investigations were prepared as following. In a typical experiment, aluminium oxide was precalcinated in air (923 K, 8–10 h), then it was exposed to water vapour for several days and evacuated at 303 K up to the constant mass. Such a surface contains proton-donating sites due to both the presence of Al–OH-groups and sorbed water molecules. This surface was dehydrated by evacuation of samples at 973 K (it had mainly Lewis sites) [3, 4].

## Results and discussion

Isotherms were measured in 273–303 K temperature interval. These isosters were constructed from these isotherms to provide the calculation differential isosteric adsorption heats. Sometimes the calculations were carried out from two isotherms by formula [5]:

$$Q_a = R\frac{T_1 T_2}{T_2 - T_1}\ln\frac{P_2}{P_1}$$

The received results in the form of dependencies of differential isosteric adsorption heat ($Q$) on surface coverage by molecules adsorbed ($\theta$) are shown on Fig. 1a, b. $\theta$ was calculated by division the value of an adsorption under the given mean of equilibrium pressure by capacity of monolayer defined from BET equation.

The results of TEA adsorption have demonstrated the irreversible character of process both for hydrated (Fig. 1a, curve 3) under $\theta < 0.4$ and dehydrated (Fig. 1b, curve 3) under $\theta < 0.6$ surfaces of alumina. It may be suggested that in this coverage interval where methods of calculation of thermodynamic characteristics for reversible processes are unacceptable, the activated adsorption of TEA with greater value of interaction energy takes place.

From Fig. 1a, curves 1–4, one can see the higher heats of TEA adsorption than those for DE, AN and *n*-pentane. Maximum on the curve of differential heats of TEA adsorption is observed at lower degrees of surface coverage ($\theta$=0.5) in difference from DE, where the maximum takes place under $\theta$=0.8. On the hydrated surface of alumina there are mainly Brønsted acidic sites with great sensitivity of TEA and DE molecules to them. For TEA, as stronger electron donor, the curve of adsorption heats is disposed higher ($\theta_{max}$=80 kJ mol$^{-1}$) than those for DE, where $\theta_{max}$=40 kJ mol$^{-1}$. Probably, the presence of these maximums may be connected with the formation of azeotropic mixtures between water molecules sorbed on the hydrated $Al_2O_3$ surface and adsorbates.

On the hydrated surface of alumina at coverages 0.2–1.0, the reversible adsorption of DE, AN and TEA molecules ($\theta$>0.4) takes place. Apparently, the electron-donating molecules form H-bonds with proton-donating sites of the surface. The higher electron-donating properties of molecules adsorbed, the higher the disposition of adsorption heats curves relative to *n*-pentane curve are, where the adsorption interaction is caused by dispersion forces.

Dehydration of pyrogenic alumina surface resulting in increasing the number of active sites with irreversible adsorption of electron donating molecules and decreasing the corresponding adsorption, heat in comparison with hydrated surface $Al_2O_3$
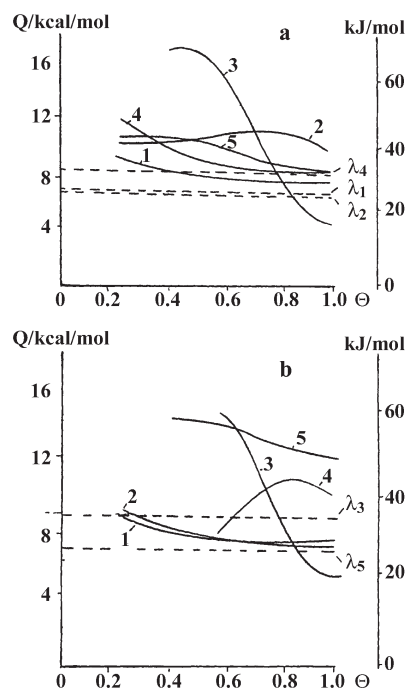


**Fig. 1** Dependencies of isosteric differential adsorption heats ($Q$) for 1 – *n*-pentane; 2 – diethyl ether; 3 – triethylamine; 4 – acetonitrile; 5 – chloroform on a – hydrated and b – dehydrated surfaces of pyrogenic alumina on the surface coverage ($\theta$). $\lambda_1$–$\lambda_5$ are condensation heats for respective adsorbate molecules

(Fig. 1b, curves 2–4). So, the degree of surface hydration has great influence on the active sites properties.

Thermodynamic studies of chloroform adsorption as molecule-sound showed the reversible adsorption of $CHCl_3$ in monolayer region for hydrated sample of $Al_2O_3$ (Fig. 1a, curve 5) occurs. When the value of the interval of coverage has achieved $\theta = 0.35-0.55$, adsorption heats remain constant, which is testified by the uniform of the adsorption sites with the interaction energy 45 kJ mol$^{-1}$. Furthermore, with adsorption value increasing, adsorption the heats are falling down, approaching to the condensation heats.

On the dehydrated surface (Fig. 1b, curve 5) irreversible $CHCl_3$ adsorption takes place at $\theta < 0.4$, showing the strong adsorbent–adsorbate interaction. Here, also the independence of adsorption heats from surface degree of coverage is observed at $\theta = 0.4-0.6$ but the interaction energy of these sites is higher and to amounts 60 kJ mol$^{-1}$. It is known [2] that two types of basic sites on the alumina surface exist. OH-groups, which are weak sites, and the strong basic sites – bridge oxygen atoms M–O–M. We have suggested, that in our case these strong basic sites are situated in the irreversible chloroform adsorption region, where, because of irreversibility of the process, we can not calculate their energetic. The interaction energy of the weak sites amounts to 60 kJ mol$^{-1}$.

On the hydrated surface of $Al_2O_3$, the water not removed after evacuation at 303 K, screens these sites and compensates the charge on the bridge oxygen atoms, which is a reason for the decrease of the adsorption heats in comparison with dehydrated surface.

At $\theta > 0.4$ the curves of the adsorption heats of hydrated and dehydrated surfaces are very much alike and almost parallel to each other. This may mean, the sorbed water in this region of coverage has no influence on the chemical nature of the surface, but only decreases the access of $CHCl_3$ molecules to active sites.

So, the investigations carried out showed the presence of the active sites on the surface, on which irreversible adsorption of electron-donating molecules and $CHCl_3$ takes place and the dependence of energetic properties of the surface from electronic structure of adsorbate, quantity of substance adsorbed and degree of surface hydration. On the hydrated alumina, the adsorbed water molecules screen the active sites, which results in changing adsorbent–adsorbate interaction and increasing the adsorption of organic bases and CH-acids in the region of irreversible adsorption.

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