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MECHANISM OF H_2O VAPOR ADSORPTION IN A TYPE ZEOLITES. THE ADSORPTION ISOTHERMS

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Abstract: In this study, the energy characteristics of water vapor adsorption in NaA and NaA($NaBO_2$) zeolites were measured by adsorption calorimetry. Information of differential heats, isotherms, entropy and kinetic of adsorption in the matrix of NaA and NaA($NaBO_2$) zeolites were obtained. Adsorption isotherms (a) and differential heats of adsorption (Q_d) of water vapor by NaA and NaA($NaBO_2$) zeolites were measured at 303 K. The heats of adsorption are stepwise and each step corresponds to the stoichiometric formation of adsorption complexes of H_2O molecules with Na^+ or H^+ ions, $(H_2O)_n/Na^+$ or H^+, (n = 1-4), which are located on the S_{III}, S_{II} and S_I crystallographic positions of NaA and NaA($NaBO_2$). Hydration mechanism of NaA and NaA($NaBO_2$) are complex and at saturation, the zeolites are occupied by the next water zeolitic host/guest systems: NaA – 2.2[$(H_2O)_4/Na^+_{III}+H^+$], 3[$(H_2O)_2/Na^+_{II}$] and 6.6[$(H_2O)_2/Na^+_I$]; NaA($NaBO_2$) - 2[$(H_2O)_4/Na^+_{III}$], 3[$(H_2O)_4/Na^+_{II}$] and 6.86[$(H_2O)/Na^+_I$]. The complete hydration of the α- and β cages of NaA amounts thus to 21,8 and 6,2 respectively H_2O/u.c. and α-cage of NaA($NaBO_2$) – 26,3 H_2O/uc. The mean molar integral adsorption entropy of water is ~-30,5 J/mol K less than the entropy of the bulk liquid. This value nearly the same as entropy of crystalline water so the mobility of water in the zeolitic matrix is solidlike.

Keywords: zeolite, adsorption, isotherm, molecular sieves, NaA, NaA($NaBO_2$) - Sodium metaborate, host-guest interactions, water vapor, adsorption calorimetry.

Introduction. All zeolites serve the purpose of selectively adsorbing smaller molecules from larger ones; however, it is imperative to choose the right zeolite for a specific application. Type A zeolites have distinct capabilities of adsorption by offering ion exchanges, whereas Type X frameworks have a different shape and offer much larger pore openings than the former. Type A zeolites are synthetic, hydrous, alkali aluminosilicates, with exceptionally advantageous structural channels and cavities. [19].

Interest in zeolite molecular sieves has increased over the past few years due to advances in oil refining, oil and gas purification, and agricultural applications.

An adsorption isotherm is a plot of the amount of adsorbate (e.g. gas, liquid, or solute) adsorbed per unit mass of adsorbent (e.g. porous material) as a function of the equilibrium partial pressure (for gases) or concentration (for liquids and solutes) at a constant temperature. The adsorption isotherm is typically measured using a variety of experimental techniques, including gas adsorption (e.g. using the BET method), liquid adsorption (e.g. using the Langmuir method), and chromatography (e.g. using the Freundlich method).[20]

Adsorption isotherms provide important information about the thermodynamics and kinetics of adsorption. Specifically, they can tell us:

The type of adsorption: Adsorption isotherms can be classified into different types based on the shape of the curve. For example, the Langmuir isotherm is a type of adsorption isotherm that describes a monolayer adsorption process, while the Freundlich isotherm is a type of adsorption isotherm that describes a multilayer adsorption process.

The extent of adsorption: Adsorption isotherms can tell us the maximum amount of adsorbate that can be adsorbed per unit mass of adsorbent at a given temperature and pressure/concentration. This is important for designing adsorbent materials for specific applications.[20]

The strength of adsorption: Adsorption isotherms can tell us the strength of the interaction between the adsorbate and the adsorbent. This is important for understanding the thermodynamics of the adsorption process and for designing materials that have high selectivity for specific adsorbates. [20]

The rate of adsorption: Adsorption isotherms can provide information about the kinetics of the adsorption process, including the rate at which the adsorbate molecules are adsorbed onto the adsorbent surface. [20]

How do we interpret adsorption isotherms?

Interpreting adsorption isotherms requires an understanding of the physical and chemical properties of the adsorbent and the adsorbate. Here are some key points to consider when interpreting adsorption isotherms: [20]

Type of adsorption: As mentioned earlier, the shape of the adsorption isotherm can provide information about the type of adsorption that is occurring. For example, a Langmuir isotherm indicates that the adsorption is limited to a single layer, while a Freundlich isotherm indicates that multiple layers of adsorbate are forming on the adsorbent surface. [20]

Maximum adsorption capacity: The maximum amount of adsorbate that can be adsorbed per unit mass of adsorbent is an important parameter for designing adsorbent materials. The maximum adsorption capacity can be calculated from the plateau of the adsorption isotherm.

Strength of adsorption: The strength of the interaction between the adsorbate and the adsorbent can be determined from the shape of the adsorption isotherm. A steeply rising adsorption isotherm indicates strong adsorption, while a shallow slope indicates weaker adsorption. [20]

Materials and Methods. The focus of this chapter is single-crystal adsorption calorimetry, which is used for the direct measurement of adsorption energies on well-defined surfaces, both single- and poly-crystalline. The method was pioneered in the 1990s mainly by D.A. King and C.T. Campbell and is based on earlier work by S. Černy. Especially in recent years, the technique has seen increasing proliferation and development. In contrast to desorption-based methods, such as temperature-programmed desorption and isosteric measurements, calorimetry is also well suited for irreversible reactions. The systems studied range from simple adsorption of small

molecules, such as CO and NO, to surface reconstructions, reaction intermediates, hydroxyl group formation, metal adsorption and diffusion into polymers, particle-size dependent adsorption energies on model catalysts and even electrochemical reactions on electrode surfaces in the liquid phase.

Differential molar adsorption calorimetric studies of water adsorption in NaA zeolite were carried out using the device described in [14, 15, 18]. The use of the method of compensation of heat fluxes by the Peltier effect made it possible to increase the accuracy of measuring the heat of adsorption. Adsorption measurements were carried out on a unique high-vacuum volumetric setup, which made it possible to carry out adsorption measurements and dosing of the adsorbate with high accuracy. The NaA zeolite used for this study is a synthetic binder-free zeolite. Zeolite NaA($NaBO_2$) was obtained by the hydrothermal method [16] and kindly provided by Dr. J.C. Buhl from the University of Hannover. Before the inlet of water vapor, the sample was warmed up and subjected to high-vacuum pumping at 450°C for 10 hours. Before measurements, the water was carefully purified.

Results and Discussion. Figure 1 shows the adsorption isotherms at 303K of water in NaA (1) and NaA($NaBO_2$) (2) extending to ~10 -6 of relative pressure p/p 0 (p 0 is the vapor pressure of water, p 0 (303 K) = 4.24 kPa, Handbook of Chemistry and Physics, 1975 [17]. The adsorbed amount, expressed in the unit H_2O per unit cell (u.c.), was calculated from the experimentally determined quantity a/mmol according to N/H_2O per u.c. = ka/mmol/g with k = 1,7 and 1,77 for NaA and NaA(BO_2), respectively, taking into account the differently molar masses. Starting with a convex shape, the adsorption isotherms rise steeply from ~12,92 to ~21,93 water molecules per unit cell (u.c.) (~7,6 to ~12,9 mmol/g) (1) and from ~8,32 to ~19,29 H_2O/u.c. (~4,7 to ~10,9 mmol/g) (2). Then curves sharply turn toward the ordinate and increase linearly up to saturation.

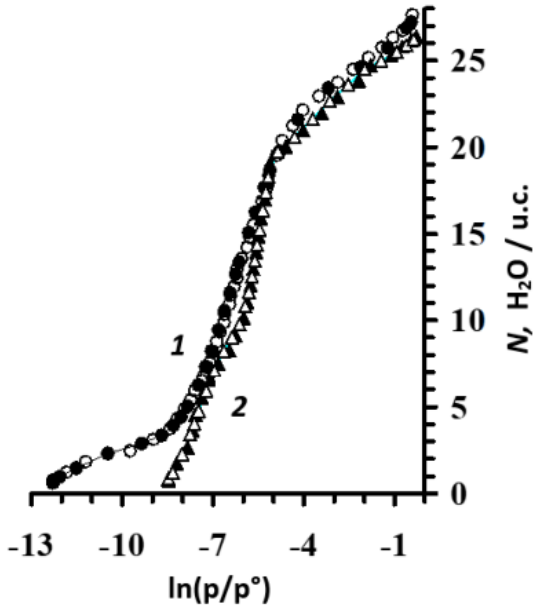

Fig. 1. Isotherm of H_2O adsorption in zeolites 1 - NaA, 2 – NaA ($NaBO_2$) at 303 K., Δ-experimental data; ●,▲-calculated using VMOT.

Conclusion. Formation of a four-dimensional complex with H^+ and Na^+ cations in position S_{III} on the τ curve in the range from 8.14 to 10.12 H_2O/u.c. characterized by a slowdown in the adsorption process. The section responsible for water adsorption in β-cavities is characterized by a small maximum at the moment of completion of adsorption in β- cavities. The difficulties experienced by a water molecule to overcome the barrier of 80 kJ/mol when penetrating through a six-membered oxygen ring in the β cavity are clearly seen in our earlier work [13]. The relatively large weight of two samples of the studied NaA zeolites (3.7 and 4.5 g) greatly slowed down the process of processing the charge with water, especially at low fillings (200-350 hours respectively). At large fillings, the process accelerated (30–40 hours), but in the region of adsorption in β-cavities, the time for establishing adsorption equilibrium τ began to slow down again and reached 65–90 hours.

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