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“Salt in a Porous Matrix” Adsorbents: Design of the Phase Composition and Sorption Properties

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Abstract—This review formulates the concept of target-oriented synthesis of two-component “salt in a porous matrix” (SPM) adsorbents designed for processes such as gas dewatering, moisture control, heat conversion in adsorption heat pumps, and equilibrium shifting in catalytic reactions. In terms of this approach, the requirements imposed on an ideal adsorbent, which is optimal for a particular application, are initially formulated; then, a material with nearly optimal properties is synthesized. Methods for the target-oriented synthesis of SPM adsorbents with the required properties are considered. The effects of the nature of the salt and the matrix, the salt content, the pore size of the matrix, and the synthesis conditions on the phase composition and adsorption properties of the SPM adsorbents are studied.

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INTRODUCTION

The development of new materials, among which adsorbents occupy an important place, is mainly responsible for scientific and technological progress. The capability of porous charcoals to absorb gases in volumes that are several times higher than their intrinsic volume was described as early as 1777 [1]. The phenomenon of adsorption is in wide current use in various industrial processes and technologies [2–7]. Adsorbents are most commonly used for the purification of gases and liquids and the separation and storage of their components. In the past decades, adsorption systems have been considered as promising systems for heat energy conversion, especially with a low temperature potential [8]. Of course, the requirements imposed on adsorbents for various applications can be dramatically different. For example, materials that can selectively absorb low concentrations of the desired gas from a mixture are required for the separation of gases. Adsorbents that exchange water vapor at a relative vapor pressure of $P/P_0 = 0.5–0.6$ are required for moisture control in museum showcases. The typical range of P/P_0 required for a relatively new application such as adsorption heat pumps is 0.10–0.35 depending on a number of conditions.

Usually, an adsorbent for a given application is chosen by searching among currently available materials developed for other purposes. This process is time consuming; although it is a palliative, it often gives an adequate solution to the formulated problem but not the best. At the same time, the current level of the development of materials science and nanotechnology makes it possible to implement a fundamentally different approach, which will be considered in this article. It

consists of the target-oriented synthesis and design of materials with adsorption properties to best meet the requirements of a particular application. This problem is formulated for ordinary (single-component) adsorbents, but the possibilities of varying the properties of two-component materials at the stage of synthesis are much broader. This opens up a number of fundamentally new opportunities, including those related to nanosize effects.

This review is devoted to two-component “salt in a porous matrix” (SPM) adsorbents in which one component is a matrix of an ordinary adsorbent (silica gel, aluminum oxide, porous charcoal, etc.), with an inorganic salt as the second component placed in the pores of this adsorbent. This salt interacts with a sorbate (water, methanol, or ethanol vapor and ammonia) to increase the sorption capacity [9–11]. The salt can be referred to as an active component of the composite (by analogy with supported catalysts). The introduction of a salt can result in fundamentally new properties of the composite, which were mainly related to monovariant equilibrium between this salt and a gas. The role of the porous matrix is also of importance. This matrix not only absorbs an adsorbate but also serves as a dispersion medium, which forms a required salt particle size and a high salt surface area, affects the state and properties of the salt, and provides heat supply through the solid phase and gas transport through the pore system. This review surveys the physicochemical fundamentals of the target-oriented synthesis of SPM adsorbents and the properties and applications of these adsorbents.

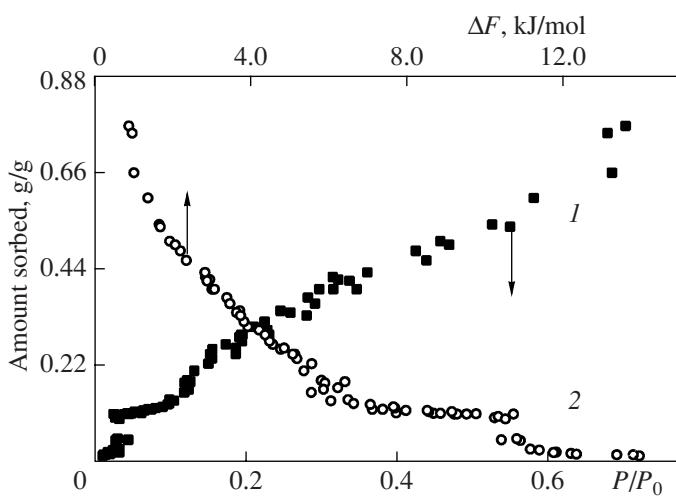


Fig. 1. Dependence of the equilibrium adsorption of water on SSV-1K on (1) relative humidity and (2) adsorption potential.

PHYSICOCHEMICAL FOUNDATIONS OF THE TARGET-ORIENTED SYNTHESIS OF SPM ADSORBENTS

Although considerable advances have been made in the development of adsorbents and adsorption technologies, these materials and technologies can be really improved. First, this can be performed by maximally approximating adsorbent properties to the requirements of a particular process, that is, by increasing adsorbent efficiency. The problem of the target-oriented synthesis (design) of materials with specified adsorption properties can be separated into the following two parts: (a) the determination of requirements imposed on an ideal adsorbent, whose properties are optimal for the given application and (b) the synthesis of a real adsorbent with properties identical or similar to the properties of an optimum adsorbent.

Below, we will formulate the main requirements imposed on adsorbents for several practically important applications. In an analysis of these requirements, we will use the Polanyi principle of temperature invariance [12]. According to this principle, the degrees of filling of the adsorption space with an adsorbate at different temperatures T_a and T_b are equal at gas pressures P_a and P_b related by the equation

$$T_a \ln h_a = T_b \ln h_b, \quad (1)$$

where $h_a = P_a/P_0(T_a)$ and $h_b = P_a/P_0(T_b)$ are relative sorbate pressures and P_0 is the saturated vapor pressure of an adsorbate at the adsorption temperature. This universal principle can be applied to both microporous and mesoporous adsorbents [13–15]. Therefore, in the subsequent consideration, we believe that adsorption on an optimum adsorbent is a single-valued function of the adsorption potential $\Delta F = -RT \ln h$ and formulate requirements for this adsorbent in terms of ΔF , that is,

in the general form, which is independent of the particular adsorbent–adsorbate pair.

Another approach can be expressed in terms of the shape of the adsorption isotherm (isobar) of an optimum adsorbent. Although attention is focused on an analysis of thermodynamic criteria in this section, we will also discuss requirements for the dynamic properties of an optimum adsorbent.

REQUIREMENTS FOR AN OPTIMUM ADSORBENT

Gas Drying

The drying of process gases is a large-scale application of adsorbents because it is widely used in chemical, gas, petroleum refining, and food industries. Drying is usually performed in a flow adsorber with the regeneration of an adsorbent by heating at regular intervals. The main selection criteria for an adsorbent are a high adsorption capacity, a low dew point of the exit gas, and a low regeneration temperature.

If we restrict ourselves to a thermodynamic analysis and assume that the adsorption front is stepwise, the maximum adsorption capacity A_{\max} can be directly obtained from an equilibrium curve of sorption represented in the adsorption–relative pressure $h = P_b/P_0(T_b)$ (or adsorption potential $\Delta F = -RT_b \ln h_b$) coordinates, where T_b and h_b are the temperature and relative humidity of air, respectively, at the adsorber inlet. Figure 1 shows these dependences for an SPM adsorbent: calcium chloride in the pores of KSK silica gel (SSV-1K). At $h_b = 0.4$ – 0.5 , the maximum capacity was 0.4–0.5 g of water per gram of the adsorbent, whereas it was as high as 0.6 g/g at $h_b = 0.6$. In a real adsorber, the sorption front is not stepwise, but has a width of ΔL . However, in a sufficiently long adsorber ($L \gg \Delta L$), the dynamic capacity can be close to A_{\max} . A high capacity at the potential $\Delta F = -RT_b \ln h_b$ that corresponds to conditions at the adsorber inlet in the course of drying can be reached by the additional absorption of water by the salt introduced into the pores of an ordinary drying agent [16].

For adsorbents that obey the Polanyi rule, the limiting dew point of dried air and the regeneration temperature are related by Eq. (1), where T_a and h_a are the temperature and relative humidity of dried air, respectively, and T_b and h_b are the temperature and relative humidity of air passed through an adsorbent bed at the stage of regeneration. It is important that the moisture amount A_r that remains in the adsorbent at the adsorption potential $\Delta F = -RT_b \ln h_b$, which corresponds to conditions at the adsorber inlet in the course of regeneration, should be as small as possible. Thus, the salt introduced into the pores should not only retain a large amount of water but also readily give up it. Then, the optimum adsorbent for gas dewatering in a flow adsorber with thermal regeneration will have a maximum difference between the adsorptions A_{\max} and A_r at the values of ΔF that cor-

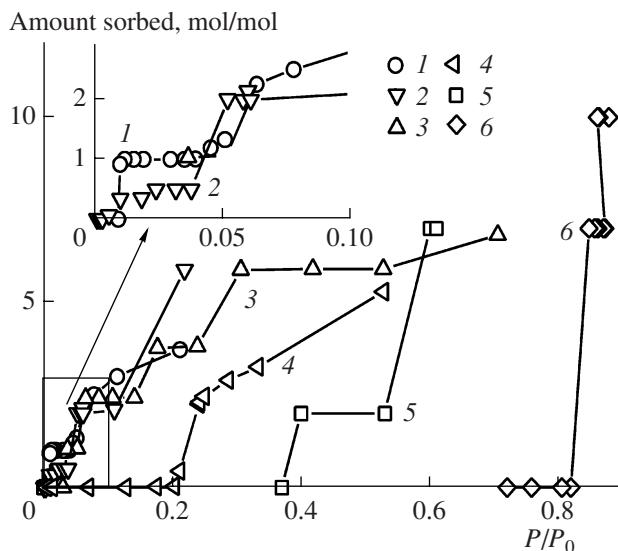


Fig. 2. Regions of occurrence and mutual transitions of the crystal hydrates of bulk salts: (1) LiBr, (2) CaCl₂, (3) MgSO₄, (4) Ca(NO₃)₂, (5) Na₂HPO₄, and (6) Na₂SO₄.

respond to conditions at the adsorber inlet in the course of drying and regeneration, respectively. Note that the requirements imposed on the optimum adsorbent will differ from those described above with the regeneration of the adsorbent by pressure release.

Moisture Control

The relative humidity of air (RH) is one of the most important parameters that should be controlled in a number of processes, for example, in the manufacture and storage of paper, wood, plastics, leathers, food products, and biological materials. Rigid requirements on RH should be met in the exposure, storage, and transportation of museum pieces, library items, and archival documents (usually, 50–60%) [17]. Here, we discuss the possibility of moisture control with the use of adsorbents in passive hydrostats. For this purpose, an optimum adsorbent absorbs and retains excess moisture as the moisture content increases above a required value or releases the sorbed moisture into a gas phase as the moisture content decreases below a required value to prevent this decrease. It is evident that the adsorption isotherm of water at process temperature T_p for this optimum adsorbent should be stepwise, and the step of sorption should occur at a pressure P such that the required relative humidity is $[P/P_0(T_p)] \times 100\%$. This is possible only if the water–adsorbent system is monovariant; this is characteristic of the formation of inorganic salt hydrates $S \cdot nH_2O$, in which a salt (S) can be simultaneously bound to a large number n of water molecules:

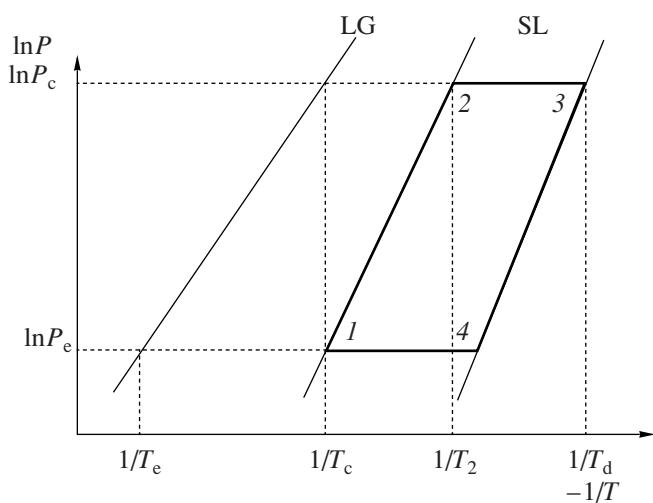


Fig. 3. Ideal cycle of an adsorption heat pump. Lines LG and SL describe the liquid–gas and sorbent–liquid equilibria, respectively.

At a fixed temperature, reaction (I) completely occurs at a threshold pressure of water vapor, and this pressure will be spontaneously maintained over the sorbent (salt). In this case, the buffer capacity of the sorbent depends on the amount of water absorbed (released) in reaction (I). For various salts, this capacity can be as high as 6–12 mol of water per mole of salt (corresponds to a sorption capacity of up to 2–3 g/g).

Conditions for the occurrence of reaction (I) are determined by the Van't Hoff equation

$$\ln P(H_2O) = -\Delta G^\circ/RT = -\Delta H^\circ/RT + \Delta S^\circ/R, \quad (2)$$

in which ΔH° and ΔS° vary over wide ranges for various salts and salt hydrates. This allows us to choose an appropriate reaction, which occurs at a required relative humidity (Fig. 2). This application usually does not place stringent requirements on the dynamics of adsorption because the characteristic process time is 1–10 h.

Adsorption Heat Pumps

Serious limitations introduced by the Montreal and Kyoto protocols [8] open a niche for adsorption heat pumps, which can play an important role in improving the environment by considerable fuel savings. The general principles of the operation of these devices were considered previously [18, 19].

An ideal cycle of adsorption heat pumps in a Clapeyron diagram consists of two isosteres and two isobars (Fig. 3). The cycle is defined by the following three temperatures: condenser temperature T_c , evaporator temperature T_e , and adsorbent dehydration temperature T_d . If all three temperatures are specified, the efficiency of the adsorption heat pump increases monotonically as the amount of pump fluid (for example, water, ammonia, and methanol) exchanged in the cycle (i.e., between the extreme isosteres of a cycle (1–2 and 3–4))

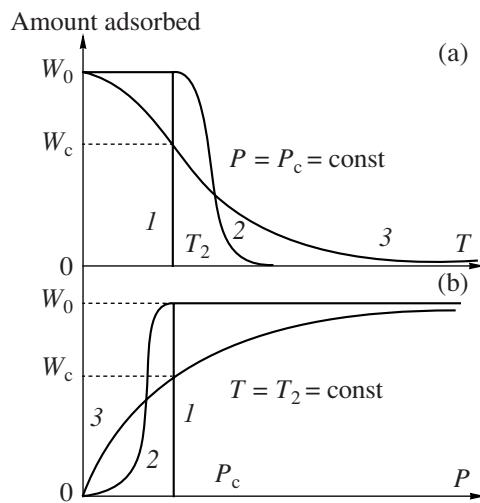


Fig. 4. Typical adsorption (a) isobars and (b) isotherms in the cases of (1) monovariant and (2, 3) divariant equilibria.

increases [20]. Because either of the isosteres is unambiguously characterized by the potential ΔF_{1-2} or ΔF_{3-4} , the optimum adsorbent for an adsorption heat pump has a maximum difference between the adsorptions of pump fluid at these two values of ΔF [20].

Other requirements are imposed on an adsorbent in the case that only two temperatures in a cycle are specified, for example, T_e and T_c . Then, the dehydration (regeneration) of the adsorbent is thermodynamically most favorable at a minimally possible temperature T_{\min} , which can be calculated from the equation $\Delta F(P_e, T_c) = \Delta F(P_c, T_{\min})$, $T_{\min} = T_c^2/T_e$. Then, the optimum adsorbent retains a maximum weight of the pump fluid at $T < T_{\min}$, and the retained fluid is removed as this temperature is reached. In other words, the isobar of desorption for this adsorbent at a pressure P_c should be stepwise (Fig. 4), which is characteristic of the monovariant salt-pump fluid equilibrium in the SPM adsorbent [20]. If the pump fluid is water, the optimum hydrate should decompose at the temperature T_{\min} (and the pressure P_c). This hydrate should be chosen among a variety of known salt compounds with water.

Upon the introduction of a salt into the pores, the kinetics of salt interaction with the pump fluid depends on mass- and heat-transfer processes rather than on the reaction between the salt and the fluid, as in the bulk state [21–23]. The desorption (adsorption) of the pump fluid (Fig. 3, stage 2–3) occurs in an adsorption heat pump by heating (cooling) the adsorbent through the metal wall of a heat exchanger with temperature $T_3 = T_d$ ($T_1 = T_c$), whereas the pressure $P_c (P_e)$ of the pump fluid over the adsorbent is maintained. As a result of combined heat-and-mass transfer, the kinetics of a nonisothermal process is exponential [21]. It is described by a linear driving force approximation [23], whereas it

obeys a diffusion model in isothermal and isobaric processes [22]. In both cases, the rate depends on the shape of the equilibrium adsorption curve in the region that corresponds to process conditions [23]. Thus, for an optimum adsorbent, the curvature of segments in an adsorption isobar that correspond to the stages 2–3 and 4–1 should decrease in the course of the process; that is, the desorption and adsorption segments should be concave and convex, respectively.

Equilibrium Shift in a Chemical Reaction

The conversion of reactants in many important catalytic processes (e.g., ammonia and methanol syntheses) is limited by the chemical equilibrium of the reversible reaction. To increase conversion, it is desirable to shift the equilibrium of such a process toward the formation of products. For example, this can be performed by removing a product from the reaction mixture by adsorption [24, 25]. The removal of the product from the adsorbent can be conveniently performed under pressure release conditions, which are easy to implement. The main requirements imposed on an adsorbent for shifting equilibrium are (a) a high capacity for the product to be removed under synthesis conditions (at a near-equilibrium product pressure P_p and a synthesis temperature T_s or at the adsorption potential $\Delta F_s = -RT_s \ln (P_p/P_0(T_s))$, where $P_0(T_s)$ is the saturated vapor pressure of the removed product at T_s , and (b) the desorption of the adsorbed product at an insignificant pressure release. Then, the optimum adsorbent should exhibit a stepwise adsorption isotherm $A(\Delta F)$, and the increase in the sorption should occur at $\Delta F = \Delta F_s$. This criterion specifies a general algorithm for searching for the required compounds (methanolates, ammoniates, etc.).

FACTORS AFFECTING SORBENT PROPERTIES

In this section, we consider the physicochemical fundamentals and methods for the target-oriented synthesis of SPM adsorbents with specified properties. To design the properties of these composites, it is necessary (a) to specify key parameters responsible for the sorption properties of these adsorbents and (b) to develop synthetic procedures with variations in the above parameters. For this purpose, we studied the physicochemical properties of SPM adsorbents and the chemical and phase composition of these adsorbents. This allowed us to understand regularities in the formation of composites, to separate key parameters, and to purposefully design the properties of SPM adsorbents.

Chemical Nature of the Salt and the Matrix

Figure 5 shows the sorption isobars of methanol and ammonia on unmodified matrices (silica gel and vermiculite) and SPM adsorbents based on salts arranged in the pores of these matrices. The introduction of a salt

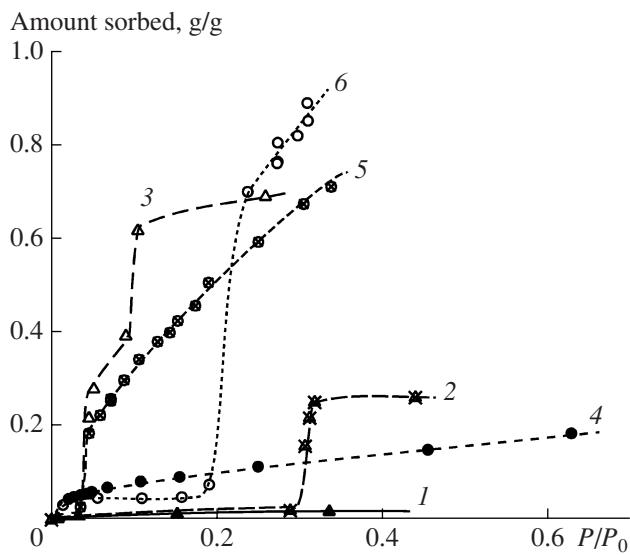


Fig. 5. Sorption isotherms of (1–3) ammonia and (4–6) methanol by (1) vermiculite, (4) KSK silica gel, and the following SPM adsorbents: (2) 41% BaCl_2 /vermiculite, (3) 63% CaCl_2 /vermiculite, (5) 29% LiBr/SiO_2 , and (6) 31% LiCl/SiO_2 .

several times increased the sorption capacity for methanol and ammonia, as compared with that of a pure matrix [10, 11]; this was also found for water [9, 26]. Consequently, the dispersed salt plays the main role in the process of sorption and its sorption properties mainly contribute to the properties of SPM adsorbents. In the sorption of gases by salts, solvates (salt and gas complexes) are formed; the thermodynamic properties of these solvates vary over a wide range (Figs. 2, 5). The monovariant character of equilibrium in this system can lead to stepwise adsorption isotherms; it was found that such isotherms are required for many applications. Thus, at the first stage of the synthesis, solvates are chosen so that the transition between them meets the above requirements imposed on an optimum adsorbent.

It was found that, upon introduction of a salt into the pores, the salt properties can change, as compared with the properties of the bulk salt, because of (a) dispersion to a small size, which is restricted by the pore walls (size effect [9–11, 27]) and (b) interactions between the salt and the matrix (host–guest effect) [28–30]. The properties of SPM sorbents can be designed and approached to the properties of an optimum adsorbent by changing the nature of the salt and using these two key effects.

Effect of the Pore Structure of the Matrix

XRD data demonstrated that a salt forms a crystalline phase in a matrix with sufficiently large pores (diameter $D_{\text{pore}} > 5$ nm), and the size of the coherent-scattering zone is close to the average pore size [9, 26,

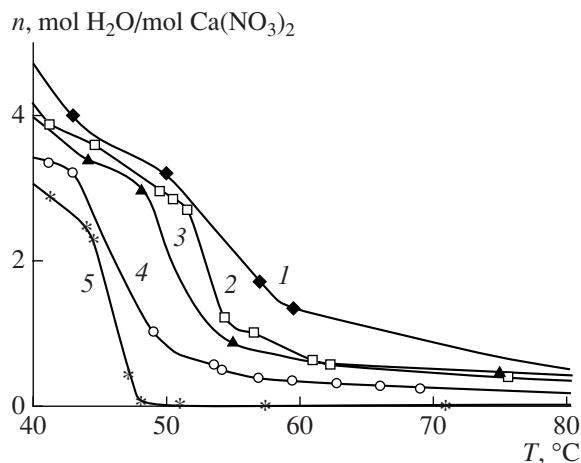
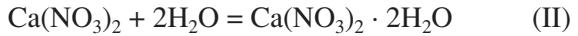


Fig. 6. Isobars of water sorption by bulk $\text{Ca}(\text{NO}_3)_2$ and the $\text{Ca}(\text{NO}_3)_2/\text{SiO}_2$ SPM sorbent with pore sizes $D_{\text{pore}} = (2) 12$, (3) 9, (4) 6, and (5) 3.5 nm.

28]. Therefore, disperse salt nanocrystals with a required size can be obtained by choosing matrices with a required pore size and a sufficiently narrow pore-size distribution. The sorption properties of the salt were found to be size-dependent. Thus, the temperature of hydration of disperse calcium nitrate



increases with decreasing pore size in silica gel (Fig. 6) [31]. This effect manifests itself at sizes of 5–50 nm. It is likely due to an increase in the contribution of surface energy to the total Gibbs energy of the salt–water system upon dispersion [32]. Another reason can be the higher mobility of water in a disperse hydrate than that in the bulk hydrate [33]. An analogous shift was found in the hydration of CaCl_2 [9]; LiNO_3 [32]; LiBr [34]; and magnesium, copper, and sodium sulfates [26] and in the formation of LiCl and LiBr complexes with methanol [35]. Upon the formation of a salt complex with ammonia, the equilibrium in pores shifted toward lower temperatures [11]. This new effect in the area of nanotechnology [27] provides the opportunity to purposefully tune up the sorption properties of SPM adsorbents to the properties of an optimum adsorbent by dispersing a salt in the pores of a matrix with a certain diameter.

Effect of the Salt Content of the Composite

The sorption capacity increases with the salt content of the composite; therefore, it is reasonable to use matrices with large pore volumes and to introduce large salt amounts into them. At the same time, limitations related to an increase in the salt volume upon the formation of a complex with a gas and a deceleration of sorbate transport should be taken into consideration [22]. Moreover, it was found that a change in the salt content can result in qualitative changes in the sorption

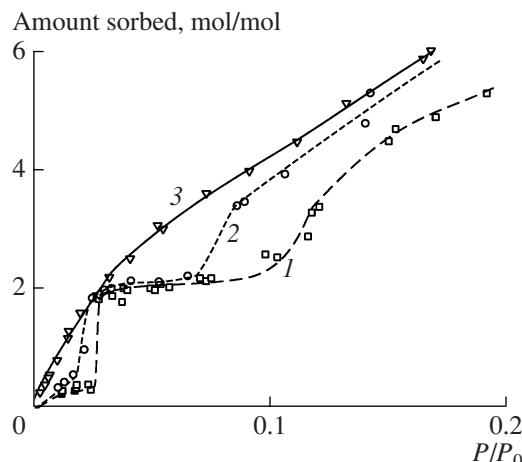


Fig. 7. Isotherms of water sorption by $\text{CaCl}_2/\text{SiO}_2$ composite sorbents with salt concentrations of (1) 33.4, (2) 23.3, and (3) 9.2 wt %.

equilibrium [28]. Thus, a change from mono- to divariant equilibrium occurred as the salt content of the $\text{CaCl}_2/\text{SiO}_2$ composite decreased from 33 to 9 wt % (Fig. 7). Initially, the plateau that corresponds to the hydrate $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ narrowed because $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ was formed at a smaller value of P/P_0 and then disappeared entirely. It is likely that the reason for this transition is the interaction between the salt and the matrix, which leads to the partial amorphization of the salt in the pores of the matrix [28].

Effect of Synthesis Conditions

The traditional procedure for the preparation of composites consists of the impregnation of a dried

matrix with an aqueous salt solution followed by water removal by heating the composite. At both stages, the salt interacts with the matrix surface to affect the phase composition and sorption properties [28]; therefore, the properties of SPM adsorbents can be purposefully affected by changing the conditions of the stages. Thus, an increase in the pH of a salt solution at the stage of impregnation qualitatively changed the sorption equilibrium of the 23.3% $\text{CaCl}_2/\text{SiO}_2$ composite with water vapor: it became divariant (Fig. 8, curves 1, 2). An increase in the composite drying temperature led to the same effect (Fig. 8, curves 1, 3).

We assumed the following mechanism for the formation of the phase composition and sorption properties of SPM adsorbents [28]. At the stage of impregnation, the adsorption of metal cations from solution on the matrix surface and the formation of $\equiv\text{Si}-\text{OM}^{(n-1)+}$ surface complexes occurred. At the stage of drying, the surface complexes affected the crystallization of the salt to cause the formation of two salt phases: amorphous surface and crystalline bulk phases. An increase in pH decreased the fraction of the crystalline phase (Fig. 9). An increase in the composite drying temperature also facilitated the amorphization of the salt phase because of the solid-phase spreading of the salt on the surface of the matrix [36, 37]. If the energy of adhesion between the salt and the matrix was greater than the surface energy of the salt, the interaction between the salt surface ions and the matrix led to the formation of a disordered amorphous salt phase on the matrix surface. The differences between the phase compositions of SPM adsorbents resulted in different types of sorption equilibria. In the sorption of vapors by composites containing a crystalline phase, crystal hydrates with a monovariant equilibrium (a stepwise shape of the isotherm of sorption) were formed (Figs. 7, 8). In the sorption of vapors by an amorphous phase, the equilibrium

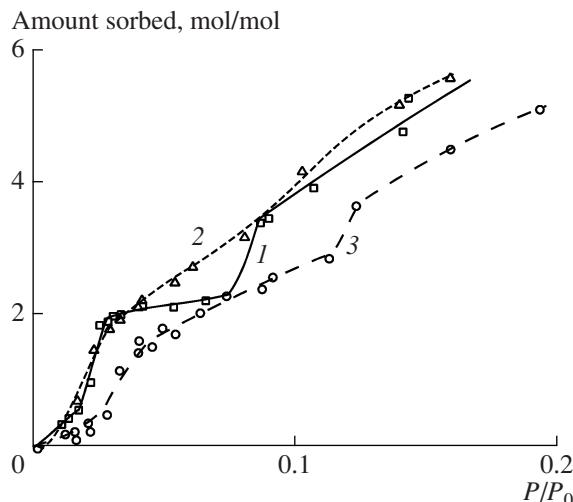


Fig. 8. Isotherms of water sorption by 23.3% $\text{CaCl}_2/\text{SiO}_2$ sorbents synthesized at pH (1, 3) 5.5 and (2) 8 and drying temperatures of $T = (1, 2) 200$ and (3) 380°C.

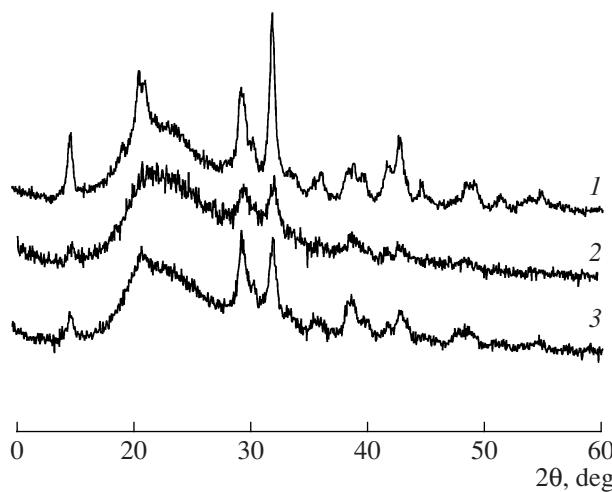


Fig. 9. X-ray diffraction patterns of 23.3% $\text{CaCl}_2/\text{SiO}_2$ samples synthesized at pH (1, 3) 5.5 and (2) 8 and drying temperatures of $T = (1, 2) 200$ and (3) 380°C.

Properties of IK-011-1 and standard drying agents

Characteristic	IK-011-1	KSM silica gel	Al ₂ O ₃
Static water capacity (RH = 45%), g/g	0.50	0.29	0.12
Dynamic water capacity, no less than, g/g	0.25	0.16	0.1
Dew point, no higher than, °C	-50	-45	-50
Regeneration temperature, °C	130–150	150	150
Dust escape in 100 cycles, no more than, %	0.5	>10	—

was divariant; this led to a smooth shape of the sorption isotherm. Thus, by varying conditions at the stages of impregnation and drying, the properties of SPM adsorbents can be designed: composites with various degrees of crystallinity of the salt in pores can be synthesized, the type of sorption equilibrium can be changed (mono-variant/divariant), and the temperature of salt–sorbate complexation can be shifted.

APPLICATIONS OF COMPOSITE ADSORBENTS

Gas drying. Based on the above concepts, an IK-011-1 commercial drying agent for gases and liquids was developed based on aluminum oxide modified with calcium chloride, which is used for the drying of process air and other gases (natural gas and acetylene) [16]. It exhibits a high dynamic sorption capacity, affords a low dew point of the dried air, and has a good hydrothermal stability (table). In the course of its development, laboratory studies of the structure and properties of the drying agent were followed by tests under industrial conditions, commercialization (at the Institute of Hydrocarbon Processing Problems, Siberian Branch, Russian Academy of Sciences), and delivery to consumers.

Humidity control. An ARTIC composite adsorbent was developed to maintain RH = 50–60%. The tests of the new adsorbent demonstrated that its capacity was higher than that of an ARTSORB commercial material by a factor of 2.5. This allows one to use it in passive hygrostats for the exposure, storage, and transportation of museum pieces and archive documents [38].

Adsorption heat engines. A family of composite adsorbents for water, methanol, and ammonia was developed for various applications: heating, air conditioning, and ice making in various climatic zones (see reviews [39, 40] and references therein). These SPM adsorbents were tested in the prototypes of adsorption refrigerators that operate using low-temperature heat sources, including solar energy.

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