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Alumina-based desiccants modified with potassium, rubidium, and cesium cations: surface properties and kinetics of adsorption

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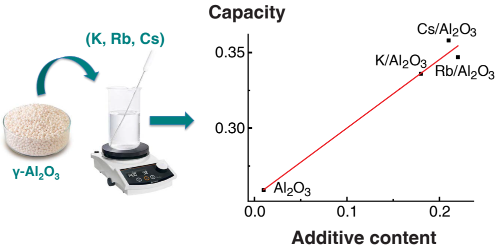
The effect of γ-Al_2O_3 modification with the cations K^+, Rb^+, and Cs^+ on its textural characteristics and acid–base and adsorption properties with respect to water was studied. The kinetics of water vapor adsorption on the test samples was described by the Gluckauf equation to model processes occurring under the influence of internal diffusion. The adsorption capacity of the modified materials was approximately 30–40% higher than that of the unmodified Al_2O_3.



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Low-temperature modifications of alumina are widely used as catalysts in isopropyl alcohol decomposition[1,2] and methanol thiolation,[3] as supports for different catalysts,[4–6] and as adsorbent desiccants for gas flows.[7–9] The influence of Li, Na, and K cations on the properties of alumina used as an adsorbent or a catalyst support was mainly studied.[5,6,10] The use of Rb and Cs cations for the promotion of catalysts for methanol thiolation[11–16] and the Knoevenagel condensation reaction[17] was reported. According to published data, one of the best adsorbent desiccants synthesized by impregnation was potassium-modified alumina.[18] The aim of this work was to synthesise mesoporous γ-Al_2O_3 modified by Rb, Cs, and K and to study the effect of the modifiers on the physicochemical properties and water adsorption capacity.

Aluminum oxide obtained from the product of centrifugal thermal activation of hydrargillite in a CEFLAR^{TM} reactor (Novosibirsk, Russia)[19] was used for alkali cation modification. After extrusion and heat treatment at 500 °C, the adsorbent grains were ground to particles 5 ± 1 mm in length and 3.75 ± 0.15 mm in diameter. The alumina was modified with potassium, rubidium, and cesium ions using wet impregnation to obtain a metal loading of 0.4 mmol per gram of the support. For kinetic tests, adsorbent granules were ground to a fraction of 0.5–1.0 mm.

According to the X-ray diffraction analysis data, all the test samples were γ-Al_2O_3. The phase ratio remained almost unchanged during the modification process (see Online Supplementary Materials, Figure S1). According to X-ray fluorescence analysis, the modified samples contained a sodium impurity, which was present in the initial sample (Table 1).

The isotherms of low-temperature nitrogen adsorption and desorption of the samples were type-IV isotherms according to the IUPAC classification. They were characterized by a sharp rise at a low relative pressure and a hysteresis loop (see Online Supplementary Materials, Figure S2). The isotherms indicated the presence of mesopores on the sample surfaces and reversible capillary condensation. Upon modifying alumina with alkali metals, its textural characteristics changed: the specific surface area (S_{BET}) decreased from 290 $m^2\,g^{-1}$ for Al_2O_3 to 193 $m^2\,g^{-1}$ for Cs/Al_2O_3, and the average pore diameter increased from 5.3 to 7.2 nm, respectively. The total mesopore volume of the modified samples was higher than that of the original (Table 1). The pore size distribution is given in Online Supplementary Materials (Figure S3). The presence of fine mesopores (2–16 nm) indicated that internal diffusion of water vapor in the adsorbent influenced the adsorption process. The original sample had a pronounced peak at 3.8 nm, and the potassium-modified sample had a broad peak at 3.7 nm and a wider distribution of fine mesopores over the volume. The samples, modified with rubidium and cesium were characterized by a polymodal distribution of fine mesopores throughout the volume of the material.

The surface acid–base properties of solids correlated with the parameters of porous materials, including moisture absorption and the adsorption capacity of the adsorbents. All the surface processes occur selectively at certain acidic or basic functional groups.[18,20]

An increase in the adsorption capacity of alumina for water vapor upon modification with Na and K cations was associated with an increase in the basic properties of the samples.[18] This was explained by the appearance of superstrong basic sites when substituting the proton at the end of the OH group with an alkali metal ion accompanied by the formation of a bridging oxygen atom between this ion and the Al^{3+} ion and a significant increase in the concentration of strong basic sites, apparently related to bridging oxygen atoms near alkaline ions. Reshetnikov *et al.*[21] showed that the introduction of sodium and potassium cations into alumina decreased the number of Lewis acid sites and increased the number of basic sites. A correlation was found

Table 1 Chemical composition and texture characteristics of alumina samples.

Sample	Additive content (wt%)	S_{BET}/$m^2\,g^{-1}_{ads}$	V_{pore}/nm	$d_{average}$/nm
Al_2O_3	0.07 Na	290	0.33	5.3
K/Al_2O_3	1.69 K	249	0.39	6.2
Rb/Al_2O_3	3.74 Rb	204	0.34	6.7
Cs/Al_2O_3	4.88 Cs	193	0.35	7.2

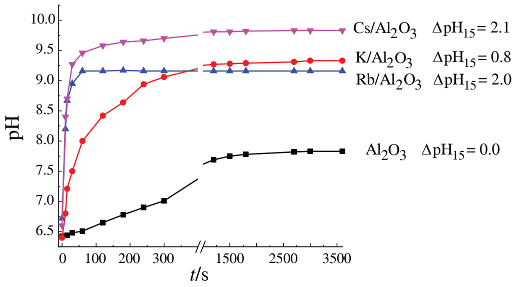

Figure 1 Kinetic curves of pH in the aqueous suspensions of the adsorbent samples.

between the equilibrium adsorption capacities of these samples and the surface acid–base properties.

Figure 1 shows changes in the acid–base characteristics of the samples as the time dependences of pH in the suspensions of the samples in twice-distilled water.

Note that the pH of the suspensions changed already in the first seconds of contact between the powder with water. At the same time, the pH change depended on the type of aprotic sites that were predominant on the surface.[22] The kinetic curves are located above the neutrality level. The value of ΔpH_{15} increased upon the transition from Al_2O_3 to Cs/Al_2O_3 (Figure 1). The most dramatic alkalization at the initial time and high values of pH_{15} were noted for Rb/Al_2O_3 and Cs/Al_2O_3, which indicated the presence of strong aprotic basic sites on their surface. The pH of the suspension in long-term contact with an aqueous medium depended on slow dissolution, hydration, and hydrolysis processes, which ultimately lead to an acid–base equilibrium in the system. The equilibrium pH value corresponds to the pH isoionic point (pH_{iip}).[23] High pH_{iip} values indicated the predominance of strong basic Brønsted sites on the aluminum oxide surface, and pH_{iip} decreased in the order $Al_2O_3/Cs > Al_2O_3/K > Al_2O_3/Rb > Al_2O_3$ (Figure 1).

The kinetics of water vapor adsorption on the modified samples was studied on a laboratory setup using the MacBain-Bakr quartz balance. The alkaline modification of the surface of initial alumina led to an increase in the adsorption capacity (a). Depending on the alkali metal used for the modification, the equilibrium adsorption capacity (a_m) increased by 30–40%, as compared to that of the unmodified adsorbent, in the order $Al_2O_3 < K/Al_2O_3 < Rb/Al_2O_3 < Cs/Al_2O_3$ (Figure S4).

It is well known that the diffusion of water vapor in adsorbent pores is the rate-limiting stage of adsorption for conventional porous adsorbent desiccants (silica gel, zeolite, and alumina). This process is usually carried out by the volume of pores and less often by their surface.[24] To describe the experimental data, we used the equation proposed by Glueckauf[25] for the kinetics of water adsorption by porous adsorbents,[26–28]

$$\frac{da}{dt} = \beta\left(a_m - a\right), \tag{1}$$

with the initial conditions $t = 0$ and $a = 0$, where t is time, s; a is the current value of adsorption; a_m is the equilibrium value of adsorption when adsorption occurs under isothermal conditions at constant partial pressure (P_0); and β is the kinetic coefficient expressing the adsorption rate constant, s^{-1}.

Equation (1) can be represented in the linear form

$$-\ln\left(a_m - a\right) = \beta t - \ln a_m. \tag{2}$$

The coefficient β can be calculated from the slope of the experimental time dependence of $\ln(a_m - a)$.

Table 2 shows the experimental values of a_m and the model parameters obtained for all the samples. The Glueckauf equation adequately described the experimental data.

The modification of the aluminum oxide desiccant with potassium, rubidium, and cesium cations increased the equilibrium adsorption capacity (a_m) with respect to water vapor by 31, 35, and 38%, respectively, as compared to that of the unmodified desiccant.

Table 2 Kinetic characteristics of the adsorbents (Glueckauf equation parameters).

Sample	a_m/g g_{ads}^{-1}	β/s^{-1}	R^a
Al_2O_3	0.26	0.024	0.96
K/Al_2O_3	0.34	0.022	0.93
Rb/Al_2O_3	0.35	0.019	0.95
Cs/Al_2O_3	0.36	0.017	0.97

[a] R is linear correlation coefficient.

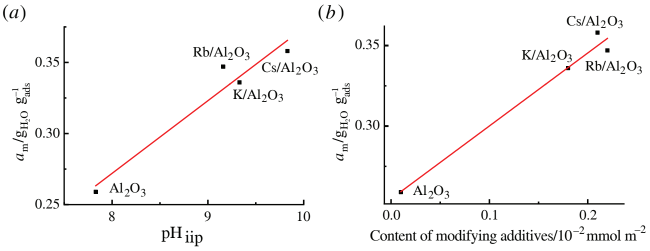

Figure 2 Water vapor adsorption capacity *versus* (*a*) pH_{iip} and (*b*) the content of modifying additives in the test samples.

We found that the equilibrium water vapor adsorption correlated well with the value of pH_{iip} [Figure 2(*a*)] and the content of additives in the samples per unit surface area [Figure 2(*b*)].

Thus, we found that, in the modified samples of alumina (γ-Al_2O_3), the specific surface areas decreased and the mesopore diameters increased in the following order: Al_2O_3, K/Al_2O_3, Rb/Al_2O_3, and Cs/Al_2O_3. The kinetics of water vapor adsorption on the test samples can be described by the Gluckauf equation used to model adsorption processes occurring under the influence of internal diffusion. An increase in the adsorption capacity of the materials for water vapor correlated with the surface acid–base properties. The sample modified with cesium (Cs/Al_2O_3) had the highest adsorption capacity for water vapor, which exceeded the capacity of the unmodified γ-Al_2O_3 by 40%. This fact allowed us to consider cesium as a promising metal cation for modifying alumina in order to obtain effective adsorbent desiccants.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7669.

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