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Sorption of carbon dioxide by the composite sorbent "potassium carbonate in porous matrix"

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Sorption of CO_2 in the presence of water vapor by the K_2CO_3—γ-Al_2O_3 composite sorbent was studied by IR spectroscopy *in situ*, X-ray diffraction analysis, and the differentiating dissolution method and reasons for a decrease in its dynamic capacity are given. The samples containing $K_2CO_3 \cdot 1.5H_2O$ in pores are characterized by the maximal dynamic capacity. A mechanism for CO_2 sorption was proposed, which qualitatively explains the obtained dependence of the capacity on the water content in the composite sorbent. A high dynamic capacity can be maintained by regeneration of the sorbents by water vapor at 170 °C. The capacity of the sorbents decreases during the first 10 sorption—regeneration cycles due to the formation of an inactive phase of potassium aluminum carbonate.

Key words: composite sorbent, chemisorption, carbon dioxide, potassium carbonate, IR spectroscopy *in situ*.

The problem of CO_2 sorption by solid sorbents at ~100 °C under conditions of a high moisture content in the gas mixture is of basic significance for the creation of adsorption systems for CO_2 removal from flue gases. The capacity of conventional microporous sorbents based on the zeolites or activated carbons toward CO_2 decreases in a wet atmosphere and at temperatures higher than 40 °C, which makes their use inefficient.[1] One of the most promising sorbents for CO_2 extraction from flue gases is the potassium carbonate—porous matrix system, proposed earlier by several groups of researchers.[2—6] In particular, the potassium carbonate—porous carbon sorbent, whose dynamic capacity before the onset of the breakthrough in a flow-type absorber is ~30 mg CO_2 g^{-1} of sorbent, has been described.[3,7,8] The sorption of CO_2 results in the transformation of potassium carbonate into hydrocarbonate

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2\,KHCO_3,$$

and at temperatures higher than 150 °C the equilibrium shifts substantially toward reactants. This sorbent possesses a high dynamic capacity only when the salt introduced into the matrix pores exists in the form of hydrate $K_2CO_3 \cdot 1.5H_2O$. To achieve such a phase composition, the composite is regenerated before sorption by steam at 150 °C.[3]

It is difficult to use this sorbent in practice because of its low dynamic capacity. In fact, the high porosity of activated carbons (~0.4 g cm^{-3}) results in the situation that the dynamic capacity per sorbent volume unit is only 11—13 mg cm^{-3}. Such a composite material can be used only in very large adsorbers.

It has previously been shown[9,10] that in another composite system, *viz.*, K_2CO_3—γ-Al_2O_3, the dynamic capacity toward CO_2 as high as 90 mg g^{-1} can be reached, although this index decreases considerably already after the first regeneration.[11,12] The present work is an attempt to study the mechanism of CO_2 sorption by the K_2CO_3—γ-Al_2O_3 system and to reveal reasons for decreasing dynamic capacity of these sorbents.

Experimental

The supporting matrix was γ-Al_2O_3 produced at the ONPZ plant (Omsk, Russia) with a pore volume of 0.7 g cm^{-3} and a specific surface area of 220 m^2 g^{-1}. The support was impregnated with a 40% aqueous solution of K_2CO_3. The solvent was removed by drying in a desiccator at 200 °C or on a rotary evaporator using a boiling water bath. The salt content in the completely dried sample was 26.8 wt.%. The elution sorption curves were obtained at 40 °C, passing a mixture of wet air (with the relative moisture content about 90% at ~20 °C) and CO_2 (CO_2 content 2 vol.%) through a flow-type cylindrical adsorber at a flow rate of 150 mL min^{-1}. The sorbent (4 g, ~5 mL, fraction 0.5—1.0 mm) was placed in an adsorber 6 mm in diameter and 180 mm in length. The content of CO_2 at the outlet was measured using an IR detector with a relative accuracy of ~2% in the 200—20000 ppm region. The dynamic capacity A_{dyn} was

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calculated as a ratio of the amount of CO_2 sorbed by the sorbent before the onset of the breakthrough (*i.e.*, before the sharp increase in the CO_2 content at the adsorber outlet) to the sorbent weight. The temperature plot of the dynamic capacity in the 20—80 °C region was measured by maintaining a constant temperature of the adsorbent using a water thermostat, and at higher temperatures the adsorber was placed in a furnace with automated temperature monitoring.

IR spectra were recorded on a FTIR-8300 spectrometer (Shimadzu) in the 700—6000 cm^{-1} with a resolution of 4 cm^{-1}. Before recording spectra, samples were pressed to give pellets with ρ = 20—30 mg cm^{-2}, using CaF_2 as diluent, with the sample content 10—20%. Gas sorption was studied in a flow-type steel cell with CaF_2 windows. This design of the cell makes it possible to heat pellets to 250 °C. A mixture containing 2% CO_2 and 98% N_2 was saturated with water vapor on passing through a bubbler flask and introduced to a sample with a rate of ~30 mL min^{-1}.

A Freiberg HZG-4 X-ray diffractometer with CuKα radiation and a graphite monochromator was used for detection *ex situ* of powder diffraction patterns.

Diffraction experiments *in situ* were carried out on a Siemens D-500 X-ray diffractometer using CuKα radiation and a graphite monochromator on a diffraction beam. Measurements at elevated temperatures were carried out in a special X-ray chamber.[13] A sample was placed in the chamber and heated in a He flow to 50 °C. After this temperature was achieved, a gas mixture containing 2% CO_2, 2% H_2O, and 96% He was loaded in the chamber, and after 30 min a diffraction pattern was detected. Then the sample was heated to a required temperature and stored for 30 min, and the diffraction pattern of the sample was measured again. Then the sample was cooled in a pure He flow to 50 °C, and CO_2 sorption was carried out. The heating velocity did not exceed 5 K min^{-1}. Diffraction patterns were detected in the 10°—75° (2θ) region by points with the 0.05° (2θ) step.

Differentiating dissolution was performed in the flow-type regime, passing water, a solution of HCl with pH 2, and 25% H_2SO_4 through the sample to its complete dissolution. The content of potassium and aluminum in the resulting solution was continuously measured using an atomic emission spectrometer with inductively coupled plasma to obtain kinetic curves of dissolution. Time intervals, during which a constant molar ratio of concentrations of the Al^{3+} to K^+ cations in the dissolution products is observed, correspond to the dissolved state of individual phases.[14]

Results and Discussion

It is found that conditions of synthesis have a decisive effect on the dynamic capacity of freshly prepared sorbents. For example, A_{dyn} of the sorbent prepared by calcination in air at 200 °C is several times lower than that of the sample dried on a rotary evaporator (Fig. 1). The influence of drying is mainly determined by the amount of water remaining in the sorbent after drying (Fig. 2). The maximum of dynamic activity corresponds to the formation of $K_2CO_3 \cdot 1.5H_2O$ in the matrix pores.

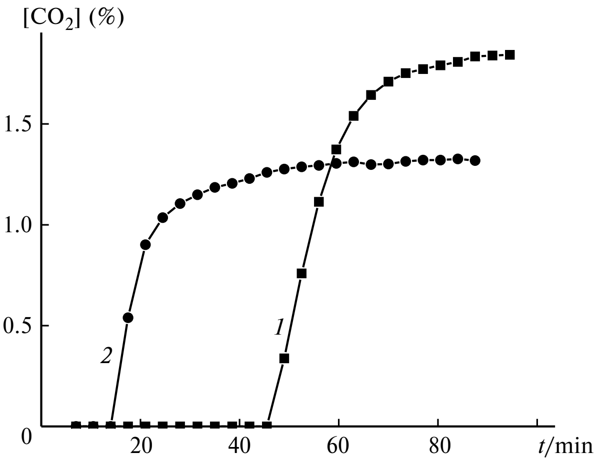

Fig. 1. Plot of the CO_2 concentration at the adsorber outlet *vs.* time for the sorbent dried on a rotary evaporator at 100 °C (*1*) and calcined at 200 °C in a desiccator (*2*). Temperature of sorption 40 °C.

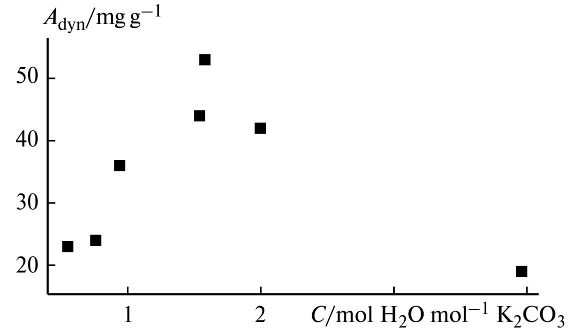

Fig. 2. Dynamic capacity of the freshly prepared samples dried on a rotary evaporator *vs.* residual water content (*C*). Temperature of sorption 40 °C.

The influence of crystallization water on CO_2 adsorption was studied by IR spectroscopy *in situ* to reveal reasons for a high dynamic capacity observed in the presence of $K_2CO_3 \cdot 1.5H_2O$ impregnated into a porous matrix. Three samples were used for the studies: sample 1 represented supported crystal hydrate $K_2CO_3 \cdot 1.5H_2O/Al_2O_3$, sample 2 was prepared by heating sample 1 at 200 °C in the reaction mixture for 30 min, and sample 3 was prepared by storing sample 2 for 30 min in an N_2 flow saturated by water vapor. In the IR spectra of samples 1—3 (Fig. 3), the intensity of the absorption band at 3200 cm^{-1}, which characterizes ν_{OH} of crystallization water, decreases in the series 1 > 3 > 2. In addition, an absorption band at 3445 cm^{-1}, which is characteristic of $KAl(CO_3)_2$, appears in the IR spectra of samples 2 and 3 (see Fig. 3).

The study of CO_2 sorption on samples 1—3 revealed the formation of intermediate compounds of the same type, *viz.*, HCO_3^- anion (1270 cm^{-1}) and dehydrated K_2CO_3 (1315 cm^{-1}) (Fig. 4). According to the data obtained, a decrease in the amount of crystallization water in the series of samples 1 > 3 > 2 decreases the maximal concentration of intermediate compounds formed upon

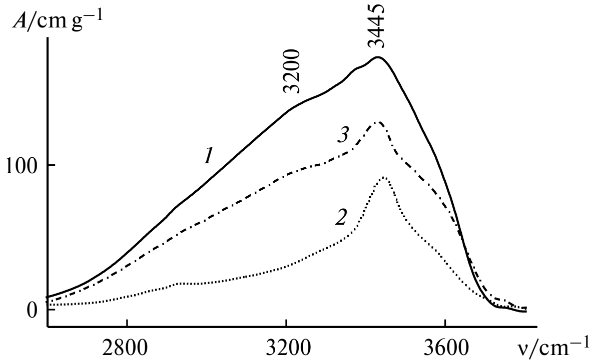

Fig. 3. IR spectra of samples 1—3 (curves *1—3*) in the region of absorption of OH groups (for conditions of preparation of the sample, see text). The integral absorption per 1 g of the sample is put on the ordinate.

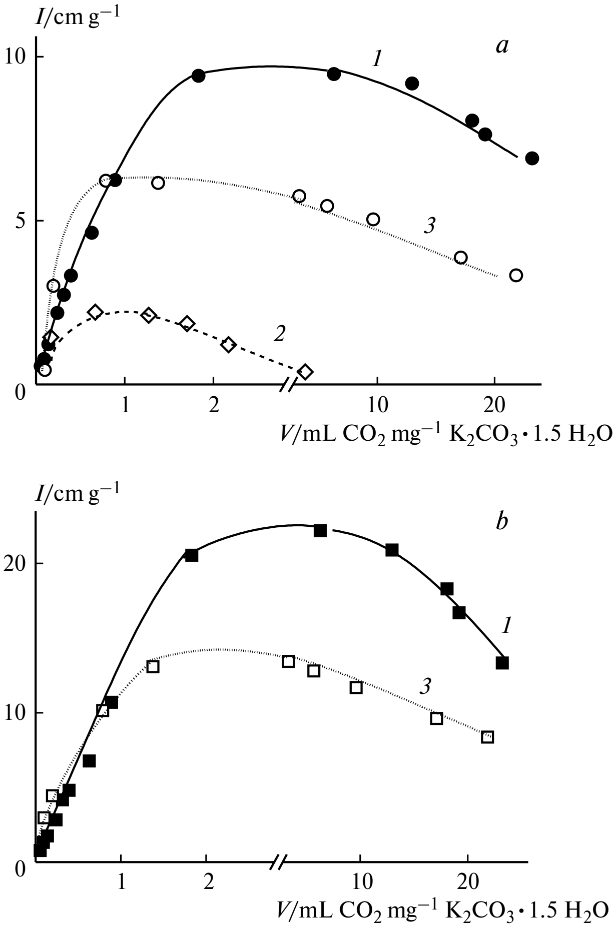

Fig. 4. Change in the integral absorption *I* (*i.e.*, difference between the initial and current values of integral sorption per 1 g of sorbent) for absorption bands at 1315 (*a*) and 1270 cm^{-1} (*b*) in the IR spectra of the samples obtained on introducing a 2% CO_2 + 2% H_2O + 96% N_2 mixture to sorbents 1—3 (curves *1—3*).

CO_2 sorption (see Fig. 4). Thus, CO_2 sorption appears to be accompanied by the insertion of its molecule into the $K_2CO_3 \cdot 1.5H_2O$ structure to form intermediate compounds, whose concentration increases first rapidly, reaches a maximum, and then decreases slowly due to their secondary transformations to form $KHCO_3$. A possible mechanism of sorption can be presented by the following scheme:

$$K_2CO_3 \cdot 1.5H_2O + CO_2 \xrightarrow{\text{rapidly}}$$

$$\longrightarrow HCO_3^- + H^+ + K_2CO_3 + 0.5\ H_2O,$$

$$HCO_3^- + H^+ + K_2CO_3 \xrightarrow{\text{slowly}} 2\ KHCO_3.$$

In the absence of a sufficient amount of crystallization water, this scheme is supplemented by the step of addition of a water molecule from the gas phase

$$K_2CO_3 + x\,H_2O \xrightarrow{\text{slowly}} K_2CO_3 \cdot xH_2O,$$

which, most likely, is the process-limiting step. The concentration of adsorbed CO_2 corresponding to a maximum of formation of intermediate compounds (see Fig. 4) correlates well with the dynamic capacity of the sorbent (*cf.* Fig. 1).

Thus, the IR spectroscopic results suggest that crystallization water bound to potassium carbonate has a decisive effect on CO_2 sorption. It is most likely that this is the "pre-dissociation" [15] state of water in $K_2CO_3 \cdot 1.5H_2O$ that favors the efficiency of the reaction with CO_2 to form the HCO_3^- anion. When the water content is higher than 1.5 H_2O molecules per K_2CO_3 molecule, a solution with a low rate of CO_2 sorption forms in the pores, and A_{dyn} of the sorbent decreases (see Fig. 2). This agrees with a low rate of CO_2 absorption by a solution of K_2CO_3. In this case, an increase in the reaction rate is achieved by the introduction of such promoters as secondary or tertiary amines into the solution or by the temperature rise.[16]

Correspondingly, the efficient regeneration of the sorbent after the sorption stage needs the formation of $K_2CO_3 \cdot 1.5H_2O$ in pores. Sorbent regeneration by steam at 150—200 °C decomposes the most part of hydrocarbonate to form $K_2CO_3 \cdot 1.5H_2O$.[3] This method for regeneration of the K_2CO_3—γ-Al_2O_3 sorbent stabilizes the dynamic capacity, which after 10 sorption—regeneration cycles reaches a stationary level of 35 mg CO_2 g^{-1} of the sorbent (Fig. 5), ~40% of the initial activity of the sorbent. It turned out that a decrease in A_{dyn} is accompanied by an increase in the weight of the dry sorbent (see Fig. 5), indicating a change in its chemical composition.

According to the X-ray diffraction data, the samples of the K_2CO_3—γ-Al_2O_3 composite sorbent contains the $KAl(CO_3)_2 \cdot 1.5H_2O$ phase, which appears at the stage of preparation when K_2CO_3 introduced into the pores interacts with the Al_2O_3 matrix (Fig. 6). The measurement in a

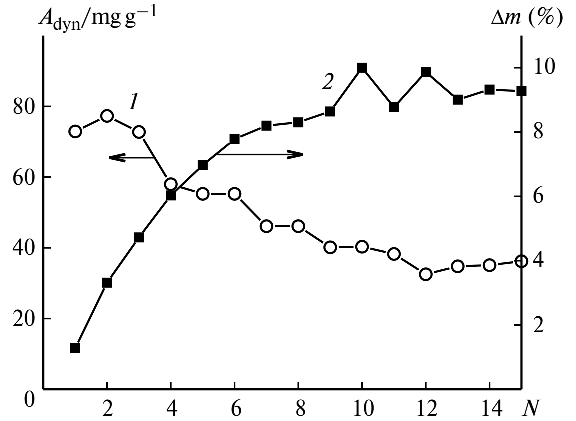

Fig. 5. Dynamic capacity of the sorbent (*1*) and the weight increment (*2*) *vs.* number of sorption—regeneration cycles (*N*). Sorption of CO_2 from wet air was carried out at 40 °C, and regeneration was carried out by steam blowing (1 atm) at 170 °C.

flow-type adsorber of A_{dyn} of pure $KAl(CO_3)_2 \cdot 1.5H_2O$ prepared by a known procedure[17] showed that this aluminum carbonate did not manifest the sorption activity toward CO_2. Therefore, upon the formation of the potassium aluminum carbonate phase a portion of $K_2CO_3 \cdot 1.5H_2O$ is transformed into the inactive form, and A_{dyn} of the sorbent decreases.

The phase distribution of potassium cations in the sorbent was studied by the differentiating dissolution method. The calculations showed that if the $KAl(CO_3)_2 \cdot 1.5H_2O$ phase incorporated in the freshly prepared sorbent contains 13% of the total amount of potassium cations in the sorbent, then after 10 sorption—regeneration cycles more than 50% K^+ cations are transferred to this phase. Further the amount of $KAl(CO_3)_2 \cdot 1.5H_2O$ is most likely stabilized (see Fig. 5) due to a decrease in the free alumina surface accessible for the reaction. The potassium aluminum carbonate phase is unstable upon prolonged storage of the samples in air and decomposes to form $KHCO_3$ (Fig. 7).

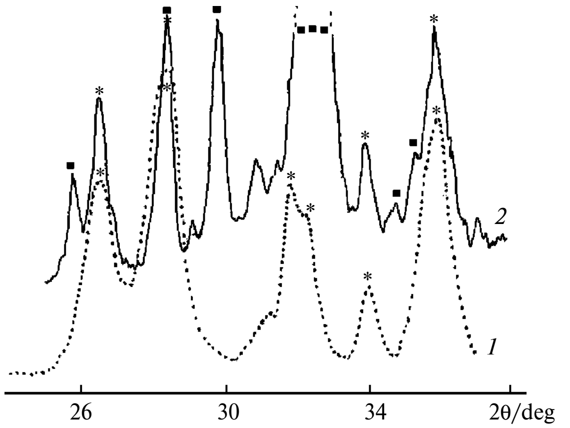

Fig. 6. Diffraction patterns of the $KAl(CO_3)_2 \cdot 1.5H_2O$ phase (*1*) and $K_2CO_3—Al_2O_3$ composite sorbent (*2*). Peaks of the $KAl(CO_3)_2 \cdot 1.5H_2O$ phase are marked by asterisks, and those of $K_2CO_3 \cdot 1.5H_2O$ are marked by squares.

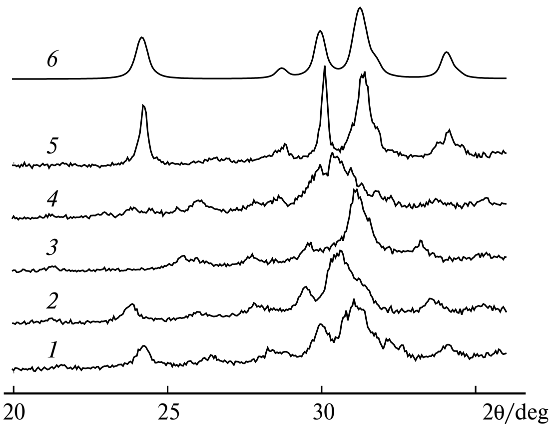

Fig. 7. Diffraction patterns of the composite sorbents (*1*—*5*) after sorption (*1*), after heating to 100 (*2*) and 200 °C (*3*), after secondary sorption (*4*), and after storage in air for 14 days (*5*) and diffraction pattern of pure $KHCO_3$ (*6*).

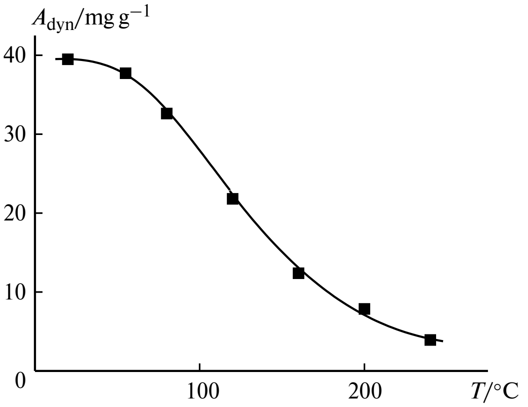

Fig. 8. Plot of the stationary dynamic capacity of the sorbent *vs.* temperature of sorption.

It is of great interest to measure A_{dyn} at different temperatures for analysis of possible practical applications of the new sorbent. The dynamic capacity of the new materials decreases fairly slowly with the temperature rise, so that even at 120 °C it exceeds 20 mg g^{-1} (Fig. 8). As the temperature increases to 200 °C, A_{dyn} decreases to 7 mg g^{-1}. Compared to the previously proposed potassium carbonate—activated carbon system,[3] the new sorbent has a substantially higher capacity per volume unit. Using a bulk density of the sorbent of 0.85 g cm^{-3}, one can easily calculate the stationary capacity (~30 mg CO_2 cm^{-3}), which is approximately 2.5-fold higher than that of the analogous system on porous carbon.

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