INTRODUCTION

The search for materials with unique sorption properties opens up new possibilities in the development of promising gas storage and separation technologies. Traditionally, the physical adsorption of gases was studied on materials with a high specific surface area and developed porosity: activated carbons, zeolites, and, more recently, carbon nanotubes and porous metal-organic frameworks. At the same time, molecular crystals of organic compounds are generally not considered as potential adsorbents since they typically form tightly packed nonporous structures [1]. Solvates of simple calixarenes are among the few examples that do not adhere to this trend. The desolvation of calixarenes under controlled conditions allows us to obtain a crystalline material with an active porous phase that absorbs gases under normal conditions [2–4]. In this work, the effect of polymorphism in the formation and thermal decomposition of the 4-tert-butylcalix[4]arene complex with acetonitrile on the formation of microporous structures characterized by substantial surface area and narrow pore size distribution was investigated.

EXPERIMENTAL

In this work, we used 4-tert-butylcalix[4]arene (α-polymorph) obtained from Fluka (4-tert-butylcalix[4]arene, purum, >97.0% (HPLC), product number 19721, CAS number 60705-62-6, lot 1242560, molecular formula C_{44}H_{56}O_{4}, molecular weight 648.91).

The experimental X-ray diffraction data were obtained on a D8 Advance diffractometer (Bruker) in Bragg–Brentano geometry with MoKα radiation (λ = 0.071 nm). The angular scanning range was 2°–20° with a step of 0.01°. A high-speed Vantec-1 counter was used. The acquisition time at each scanning point was 0.5 s.

Our investigations were performed using a DSC 204 F1 Foenix heat flow differential scanning calorimeter (DSC) (Netzsch, Germany). The calorimetric experiment was conducted in an atmosphere of dry argon of special purity grade (99.998%) at a flow rate of 25 mL/min using standard aluminum crucibles with holes in their covers. The heating rate was 10 K/min. The calorimeter was calibrated according to the melting points of five standards (mercury, biphenyl, indium, tin, and bismuth). Weighing accuracy was ±0.001 mg achieved using Sartorius M2P balances.

Thermogravimetric analysis (TGA) was performed on TG 209 F1 Iris thermomicrobalances (Netzsch, Germany) with platinum crucibles in an atmosphere of dry argon at a flow rate of 30 ml/min and a heating rate of 10 K/min.

A NOVA 1200 Series (Quantachrome) automated specific surface area and pore size analyzer was used to determine the porosity and surface area of our 4-tert-butylcalix[4]arene samples.

RESULTS AND DISCUSSION

4-tert-Butylcalix[4]arene (tBC) is a versatile compound: a host that forms clathrates or inclusion compounds with a wide array of guests [5–9]. In most solvents, tBC crystallizes with the formation of tetragonal complexes in 1 : 1 or 1 : 2 guest–host stoichiometry. Two tBC polymorphs that do not contain solvent molecules in their crystal lattices are currently known: the α-form obtained by crystallization from tetradecane, whose structure consists of tightly packed dimers in which tert-butyl groups are located in the cavities of neighboring molecules [10]; the β0-form with a low packing coefficient, obtained by sublimation in vacuum at 280°C [11], in which tBC molecules form a...
Figure 1 presents the results from DSC analysis of different BC samples (to make analysis of the curves easier, melting peaks $T_{\text{m}} = 343–344^\circ\text{C}$ are not shown). Curve 1 corresponds to the $\alpha$-form of BC; curve 2, to the $\beta_0$-form. Figure 1, 3 presents the path of two consecutive DSC curves corresponding to BC–AN complex: initial heating to $315^\circ\text{C}$ (marked by an arrow) and the repeated DSC curve after cooling the sample to room temperature. Figure 1, 4 shows the course of two consecutive DSC curves corresponding to BC–AN complex after slow heating in vacuum to $120^\circ\text{C}$ and holding it at this temperature for 3 h: initial heating to $315^\circ\text{C}$ (marked by an arrow) and the repeated DSC curve after cooling the sample to $-20^\circ\text{C}$.

Figure 1, 5 also shows the course of two consecutive DSC curves corresponding to the BC–AN complex: initial heating to $165^\circ\text{C}$ (marked by an arrow) and the repeated DSC curve after cooling the sample to $-20^\circ\text{C}$. Curve 6 corresponds to BC–AN complex after slow heating in vacuum to $220^\circ\text{C}$ and holding it at this temperature for 5 h.

The powder X-ray diffraction patterns of the investigated BC samples are presented in Fig. 2; Figure 2, 1 corresponds to the powder X-ray diagram of the $\alpha$-form of BC; Figure 2, 2, to the $\beta_0$-form; Figure 2, 3, to BC–AN complex; Figures 2, 4, 5, and 6 to BC–AN complex after slow heating in vacuum to $120, 165$, and $220^\circ\text{C}$, respectively, and holding at this temperature for 3, 4, and 5 h, respectively. Combined analysis of the DSC curves and changes in the diffraction patterns upon the heating of BC–AN complex leads us to conclude that there were structural changes caused by solvate destruction and the formation of a nonsolvated phase.

Heating a sample to temperatures above $300^\circ\text{C}$ leads to the total destruction of the BC–AN complex with the formation of non-solvated $\beta_0$-phase. This can be clearly seen from the X-ray powder diagrams (Fig. 2, 2) and the characteristic endothermic peaks on the repeated DSC curves (Figs. 1, 2–1, 4 are marked with double asterisks) corresponding to the enantiotropic polymorphic transition $\beta_0 \rightarrow \beta_0$.

At temperatures lower than $250^\circ\text{C}$, however, acetonitrile is not completely removed even after prolonged heating, as can be seen from the rather smooth endothermic peaks on the DSC curves in the range of $-120$–$250^\circ\text{C}$ and the characteristic diffraction reflections on the X-ray powder diagrams. Partial desolvation is accompanied by the formation of the thermodynamically stable $\alpha$-phase, while there is virtually no $\beta_0$-phase. This can be seen from the gradual increase in the $\alpha$-phase content when temperature and heating time rise: on X-ray diagrams, the intensity of reflection at Bragg angles $2\theta$ characterizing the $\alpha$-phase ($4.8^\circ, 5.4^\circ, 10.0^\circ$, and $10.9^\circ$) grows, while that at $10.3^\circ$ corresponding to the solvated phase diminishes. This is confirmed by the characteristic endothermic peak on

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**Diagram Description**

**Fig. 1.** DSC curves of BC samples: (1) $\alpha$-form; (2) $\beta_0$-form; (3) BC–AN complex (initial heating to $315^\circ\text{C}$ is marked by an arrow); (4) BC–AN complex after heating in vacuum to $120^\circ\text{C}$ (initial heating to $315^\circ\text{C}$ is marked by an arrow); (5) BC–AN complex (initial heating to $165^\circ\text{C}$ is marked by an arrow); (6) BC–AN complex after heating in vacuum to $220^\circ\text{C}$ and holding at this temperature for 5 h.

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bilayer-type structure with a slight shift. Upon heating BC complexes with solvents either the denser self-associated $\alpha$-form or the less dense $\beta_0$-form are formed, depending on the desolvation conditions [12, 13].

It has been proven experimentally that the $\alpha$-form of space BC, which has no guest molecules in the crystal lattice, is stable up to $250^\circ\text{C}$ [12, 14]. At higher temperatures, the less dense $\beta_0$-form becomes more stable. Upon cooling, the resulting $\beta_0$-phase does not transform into the $\alpha$-form and is metastable at temperatures lower than $250^\circ\text{C}$ (Fig. 1, curve 1). Additionally, upon cooling below $-90^\circ\text{C}$, the $\beta_0$-form undergoes a reversible phase transition into the structure described by Atwood in [15] (Fig. 1, curve 2, $\beta_0'$-form). Experimental X-ray powder diagrams of various polymorphic forms of BC are usually quite similar to the model diffraction reflections of the corresponding single crystals [14, 16]. As a result, $\alpha$- and $\beta_0$-polymorphs of BC are easily detected from their characteristic diffraction reflections and DSC curve shapes (Figs. 1 and 2).

BC–AN complex was obtained via the adsorption of saturated AN vapors onto the $\alpha$-polymorph of BC at a temperature of $25 \pm 0.1^\circ\text{C}$. The 1 : 1 stoichiometry of BC–AN solvate was confirmed by an independent thermogravimetric experiment. Desolvation of the BC–AN complex begins at $-50^\circ\text{C}$ and continues up to $-250^\circ\text{C}$; the maximum rate of mass loss was observed at $165^\circ\text{C}$, and $-85\%$ of the solvent was removed at $220^\circ\text{C}$ [17].