Deformation of Porous Adsorbents at Adsorption

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In this work deformation of activated carbon adsorbent upon CO_2 adsorption has been studied.
A model sample of the microporous carbon adsorbent was prepared from silicon carbide at 900 K by removing silicon with a chlorine flow followed by gaseous $SiCl_4$ evolution. As a result of such treatment of the silicon carbide, a high-purity microporous carbonic adsorbent was formed.
To determine the characteristics of the microporous structure, data on benzene adsorption at 293 K were processed. The following characteristics of the adsorbent sample were obtained: micropore volume $W_0 = 0.47$ cm^3/g, characteristic micropore half-width $x_0 = 0.4$ nm.
Also adsorptive deformation of Na-montmorillonite upon interaction with methanol vapor has been studied. The cation exchange capacity of the montmorillonite used was 0.801 mg-eq/g of adsorbent.
High sensitivity of the dilatometric method has been shown. The dilatometer used allowed the measurement of absolute deformations in the range $1 \cdot 10^{-7}$ to $3 \cdot 10^{-3}$ m.

1. Introduction

As early as (Meehan 1927), it was established that solid bodies change their size when adsorbing gases or vapors. Even now, however, it has not yet been generally accepted that the adsorbent is being deformed, i.e. is not inert, in the process of adsorption. Nevertheless from a physical viewpoint it can be stated that there can be no inert adsorbents at all. In fact, if we consider the simplest adsorption on the flat uniform surface of an adsorbent, even here the surface tension of the adsorbent declines when adsorbate molecules interact with the surface atoms. Thus, the uncompensated force affecting the surface atoms of the adsorbent decreases and this causes deformation of the adsorbent. It is clear that the deformation degree will be different in different cases: it depends on the properties of particular adsorptive systems. Nevertheless, even minor deformations of the adsorbents contribute considerably to the total thermodynamic characteristics determined from adsorption and calorimetry experiments (Tvardovskiy 2006). Despite this, direct measurements of adsorptive deformation essentially are not conducted nowadays.

Only measurements of structural characteristics of clay minerals (Tvardovskiy et al. 1997; Tvardovskiy et al. 1999; Tvardovskiy et al. 2019; de la Calle et al. 1988), polymeric materials (Keller et al. 1999; Zhang et al. 1997), carbons (Bangham et al. 1937; Haines et al. 1947; Wiig et al. 1949; Yakovlev et al. 2004; Fomkin 2005; Zaytsev et al. 2017) and zeolites (Krasilnikova et al. 1988) and some theoretical works (Coudert et al. 2016; Balzer et al. 2015) are performed.

For a long time the progress of research in this direction was hampered by the lack of theoretical concepts and by considerable experimental and methodical difficulties. However, studying the deformation of solids in the process of adsorption and absorption is of great importance, as mentioned, for both the progress of thermodynamics and practical applications.

This work presents the dilatometric investigations of the adsorptive deformation of some porous adsorbents. To solve this problem, an inductive-type dilatometer was used.

2. Materials and methods

An activated carbon adsorbent ACC was chosen as an adsorbent, and CO_2 was used as adsorptive. A model sample of the microporous carbon adsorbent ACC was prepared from silicon carbide at 900 K by removing silicon with a chlorine flow followed by gaseous evolution. As a result of such treatment of the silicon carbide, a high-purity microporous carbonic adsorbent was formed.

The investigations on the adsorption and deformation on the ACC are of a special interest because it contained no mesopores, and the surface of macropores was small.
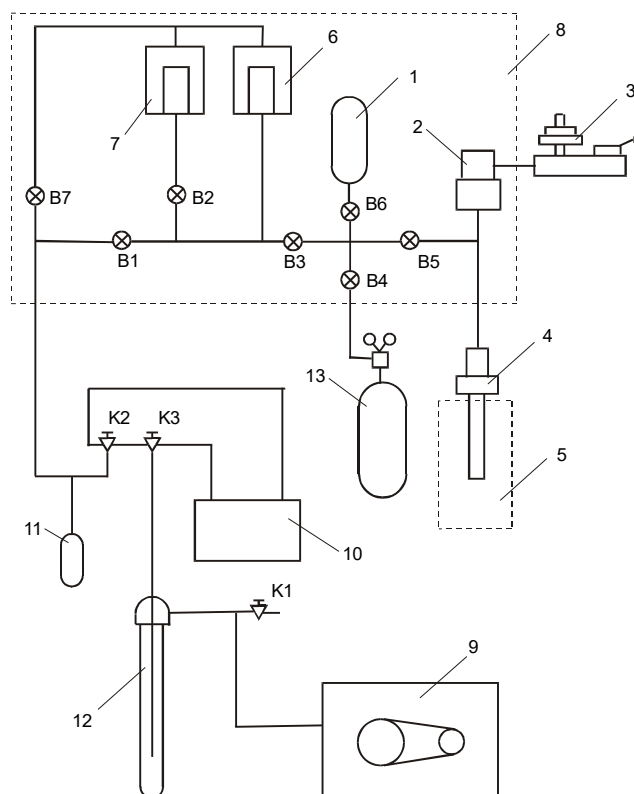

Fig. 1: Flowchart of the unit for the investigation of the adsorption and deformation of the adsorbents at high pressures. K1, K2, K3 are glass faucets; B1,...,B7 are vacuum valves; 1 is a cylinder; 2 is a zero indicator; 3 is a deadweight manometer; 4 is a dilatometer; 5 is a thermostat; 6 is a manometer M1000; 7 is a manometer M10; 8 is an air thermostat; 9 is a preevacuation pump; 10 is a diffusion pump; 11 is a thermocouple lamp; 12 is a nitrogen trap; 13 is a filling cylinder with a reducer.

A monolithic cylindrical sample with a length of 54.1 mm and a diameter of 11.4 mm was used. Before measurements, the adsorbent was evacuated for 6 h at 620 K to a residual pressure of 0.8 Pa.

To determine the characteristics of the microporous structure, data on benzene adsorption at 293 K were processed on the basis of the theory of volume micropore filling (Dubinin 1971). The following characteristics of the adsorbent sample were obtained: micropore volume W_0 = 0.47 cm^3/g, characteristic micropore half-width x_0 = 0.4 nm.

Also Na-montmorillonite from Azkamarian white bentonite was used as a adsorbent in this work. It was prepared for the experiment as follows. A 2 % clay suspension in water was prepared and mixed thoroughly with the help of a mechanical stirrer till no lumps could be found. Then the suspension was left at rest for some time. Afterwards the highest dispersion fraction was decanted with a siphon. Then purified natural specimens were treated 5 to 7 times with a 1N solution of NaCl and washed out with a distilled water until a negative reaction for chlorine ions.

The cation exchange capacity of the montmorillonite used was 0.801 mg-eq/g of adsorbent. The Azkamarian bentonite has the following crystallochemical formula:

$$Na_{0.29}K_{0.019}Ca_{0.02}(Mg_{0.31}Fe_{0.12}Al_{1.45})[Si_{3.33}Al_{0.67}O_{10}](OH)_2 \cdot 6.44H_2O \ .$$
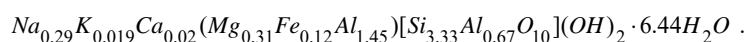
To produce non-oriented preparations shaped as tablets (height l = 5.17 mm and base diameter d_b = 8.85 mm), a pressing technique under pressure ≈ 10^9 Pa was used.

The investigations on the adsorptive deformation were carried out at a high-pressure adsorption-dilatometry unit (Fig. 1) comprising a glass part and a metallic one. The metallic part of the unit is made of a stainless steel and was tested at ≈ 25 MPa. It is designed for measurements of adsorption and deformation within a wide range of pressures and is housed in an air thermostat 8 at the temperature of 303 K (excluding the dilatometer 4

proper, the lower, adsorbent-containing section of which is housed by an individual thermostat 5). The dilatometer is directly connected to a pressure transformer 2, and connected via valve B5 to the accumulating section of the unit consisting of an accumulating cylinder 1 and a gas cylinder 13 with a reducer (or a microburet with a liquid – when the vapor adsorption was studied).

The measurements of the pressures of the gases (or vapors) under investigation within the range of 0.13 Pa – 130 kPa were conducted with the help of absolute pressure manometers. For the measurements of the pressures from 0.13 Pa to 1.33 kPa and 13 Pa to 130 kPa a bellows gauge 7 (type M10, measurements error $\pm$ 0.066 Pa) and a bellows gauge 6 (type M1000, measurements error $\pm$ 4.0 Pa) were used respectively.

Each of the manometers had a metrologic bellows of the age-hardening alloy. The bellows was connected through a rod with the differential transformer core. A generator GZ-123 sent an alternating electric current with the frequency 1000 Hz and voltage 3 V to the exciting winding of the transformer. The frequency of the alternating current supplied to the primary winding of the transformer (the exciting winding) was picked up so that to provide a substantial lowering of the stray phenomena in the course of transformation, and a high accuracy of pressure measurements. The current's voltage and frequency in the transformer's windings were measured with a digital voltmeter V7-38 and a frequency meter ChZ-36. Both manometers were calibrated at the exciting winding voltage 3 V and frequency 1000 Hz. Pressure measurements from 0.1 to 20 MPa were conducted with the help of a deadweight manometer 3, type MP-600 (precision class 0.05), with the help of the bellows pressure transformer 2. The pressure measurements were based on a compensation principle. When the gas filled the volume of the unit, the gas pressure moved the bellows bottom together with a rod of the differential transformer. This movement was recorded with the help of an electronic zero indicator. The compensation pressure was formed by the oil pressure with the help of the pump of the deadweight manometer 3 so that the bellows bottom should be positioned to the initial zero position controlled with the help of the zero indicator.

The basic part of the dilatometer (Fig. 2) was a linear differential transformer, the core of which was connected to the adsorbent by means of a rod. Any change in height of the sorbent changed the position of the transformer core, thus affecting the signal taken from its secondary winding. The calibrated dilatometer was placed in a thermostat at the test temperature and connected to the metering section (frequency meter, voltmeter, generator). The calibration was performed at a frequency of 1000 Hz. The equilibrium pressures were measured by means of M10, M1000 and MP-600 bellows gauges.

As well as in the case with the bellows gauges, the generator GZ-123 supplied the alternating electric current of frequency 1.000 Hz and voltage 3 V to the exciting winding of the transformer. These conditions provided a substantial lowering in the stray phenomena during the transforming, as well as a high deformation measurements accuracy. The voltage at the transformer windings was measured with a digital voltmeter V7-38. The electric current frequency control was performed with a frequency meter ChZ-36.

The dilatometer is designed for the adsorbent deformation measurements within the pressure interval from 0.01 Pa to 20 MPa and the temperature interval from 77 to 670 K. The measurement range for the absolute linear deformation is from $1 \cdot 10^{-7}$ to $3 \cdot 10^{-3}$ m.

The induction converter of displacements of the dilatometer was calibrated at 303 K using a set of standard plates with thicknesses of 0.01 – 1.00 mm. The dilatometer was adjusted to changes in temperature and gas pressure on a "model" of fused quartz analogous to the sorbent sample in shape and sizes.

The assembled dilatometer was connected with a metal tube to the adsorption unit of high pressure (Fig. 1).

The glass (vacuum) part of the adsorption and dilatometry unit comprised a preevacuation pump - 9; a diffusion vacuum pump - 10, a thermocouple lamp - 11 for a residual pressure control, a nitrogen trap – 12, and glass faucets - K1, K2, K3.

Valve B1 connected the vacuum portion with the accumulating portion and manometers M10, M1000, whereas valve B7 was connected with the back-pressure line of these manometers. To avoid the overcharge of the manometer M10, the valve B2 was always closed at the pressures exceeding 1.33 kPa.

The temperature (in the lower part of the dilatometer filled with the adsorbent) was determined as follows:
1) for T < 293 K – by a Dewar vessel with the substances having different melting temperatures, with the error of $\pm$ 0.2 K;
2) at T from 293 K to 373 K – by a water ultrathermostat with the error of $\pm$ 0.1 K;
3) for T > 373 K – by an electric – with the electric thermostat with the error of $\pm$ 0.3 K.
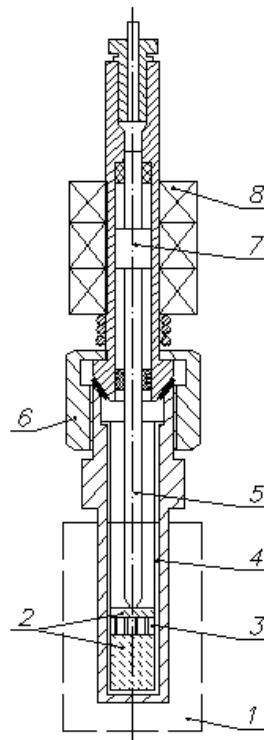
Figure 2: Dilatometric part of the unit: 1, thermostat; 2, quartz polished disks; 3, adsorbent; 4, ampoule with the adsorbent; 5, rod; 6, nut; 7, core; 8, transformer (Tvardovskiy et all. 2011)

3. Results and discussion

Fig. 3 shows dependencies of relative linear adsorbent deformation $\Delta L/L$ of the carbon adsorbent ACC on equilibrium CO_2 pressure p at temperature 243-393 K.

As follows from Fig. 3, at the temperatures $T \leq 313$ K and in the initial range of equilibrium pressures (p < 0.25 MPa) a specimen contraction reaching 0.117 % at T = 243 K can occur. At higher pressures the contraction is replaced with expansion. At the temperature of T = 393 K there can occur only adsorbent expansion with increasing pressure. With a temperature rise, the relative expansion effect proper decreases, changing from 0.575 % at 293 K to 0.283 % at T = 393 K. It is interesting to note that the dependencies of the relative linear deformation of ACC on temperature undergo an inversion which consists in a changing sequence of the curves in the initial pressure zone compared to the final one. As follows from Fig. 3, the inversion zone is located approximately in the interval 0.3 - 0.5 MPa.

Figure 4 shows the results of the experiments for Na - montmorillonite/methanol vapor system. Differential heats and isotherm of adsorption were obtained using a microcalorimeter of Calvet-type with a microbalance (MacBen-Bacre) attachment. The deformations of the adsorbents were measured with the above high-sensitivity dilatometer (Fig. 2).

It should be noted that the isotherm and the dependence of the differential calorimetric heat of adsorption on p/p_s without using the deformation curve (relative linear deformation of adsorbent) do not allow a detailed description of the processes taking place in the system.

For low adsorption values we can observe a positive deformation which is connected with the adsorption on the external surface of the sorbent, because there are practically no interlayer gaps after dehydration in montmorillonite (the only exception are the peripheral zones). Further on, after a certain opening of the structure (caused by the positive deformation) and with growing pressure, methanol molecules enter the adsorbent. Here, they can enter both the intracrystalline regions and (partially) intercrystalline ones (secondary pores). A compression or contraction of the system occurs. When analyzing this type of adsorption systems it is necessary to note that the oxygen atom in the hydroxyl group of alcohols possesses two unshared electron pairs, so the molecules of the latter, beside forming the hydrogen bonds
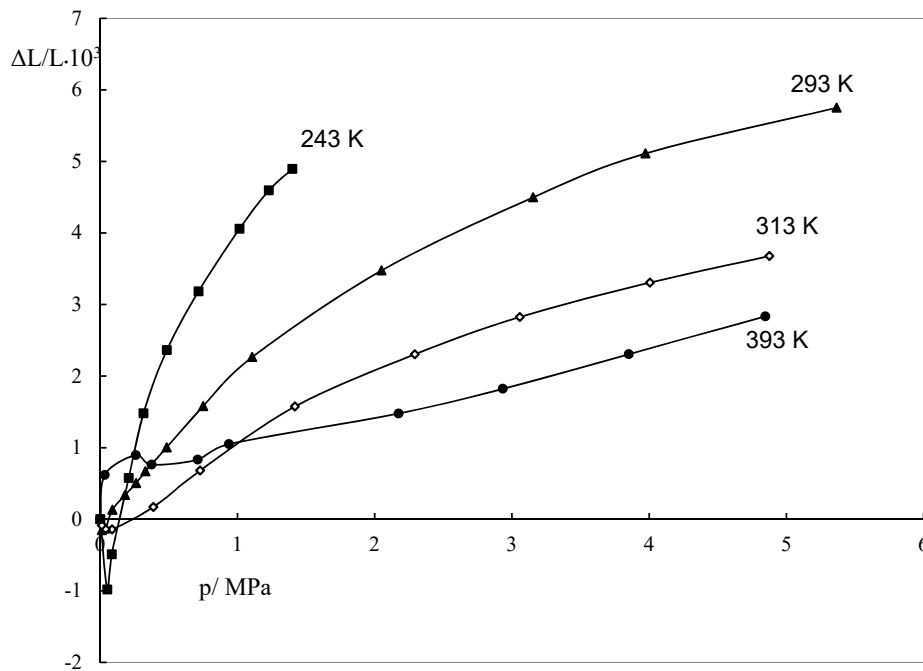
Fig. 3: Dependencies of relative linear adsorbent deformation ΔL/L on p at different temperatures (adsorptive - CO₂).
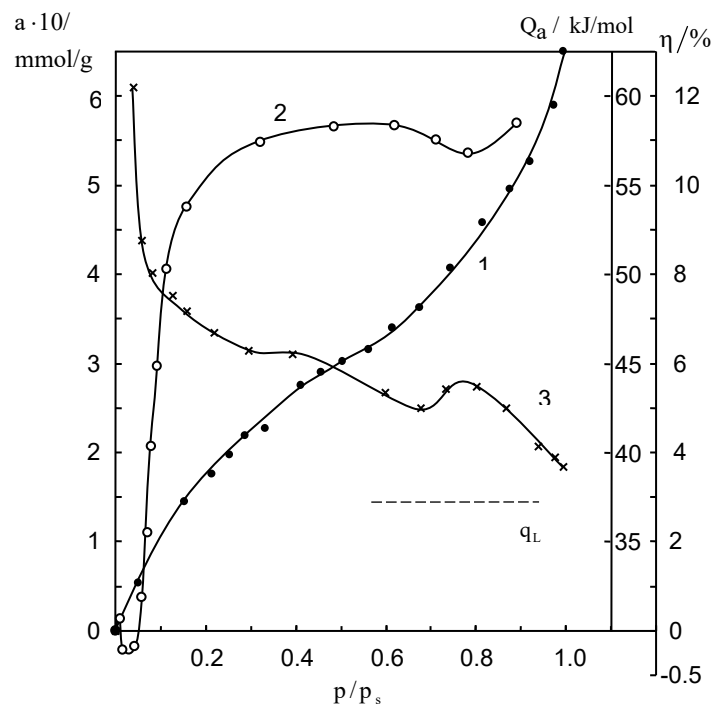

Fig. 4: Na- montmorillonite/methanol vapor system: Isotherm (1), dilatometric curve (2) and differential calorimetric heat Q_a as a function of p/p_s value (3). Temperature of experiment was 293 K.

with the surface oxygen atoms or with each other, can also specifically interact with the interlayer exchange cations of the adsorbent.

Beginning from $p/p_s \approx 0.05$, the positive adsorbent deformation occurs again, which corresponds to an abrupt decline of curve $Q_a = f(p/p_s)$. This is due namely to the system's swelling which results in a weaker field accepting the adsorbate molecules.

Figure 4 suggests that in zone $0.3 \le p/p_s \le 0.8$ values η (or $\Delta L/L$) and Q_a are practically constant. This can be caused by a "passive" filling up all vacant places in the interlayer gaps. At $p/p_s \approx 0.79$ the compression (contraction) of the system occurs, which is accompanied with a small increase in Q_a. At this point there finishes the monolayer generation in the interlayer gaps of the adsorbent. The further increase in the values of adsorption, deformation and decrease in the value of heat Q_a show that a slight swelling of the adsorbent can proceed further. Work (Tarasevich et.al. 1975) investigated the adsorption of methanol vapors by a Pyzhevsk montmorillonite, including X-raying. The latter showed that this adsorption system features the formation of a single molecular layer of methanol in the interlayer gaps of the adsorbent.

4. Conclusions

Deformations of activated carbon adsorbent ACC upon CO_2 adsorption and deformations of *Na* - montmorillonite upon methanol vapor adsorption have been studied. To solve this problem, a dilatometer was used. Its main part was a line differential transformer, the core of which was connected to the adsorbent by means of a rod. Any changes in the adsorbent height caused a change in the core position in the transformer, which influenced the signal recorded from its secondary winding. Some of the results were compared with the adsorption isotherms, calorimetry (a Calvet – type microcalorimeter with a microbalance attachment was used). High sensitivity of the dilatometric method has been shown. The dilatometer used allowed the measurement of absolute deformations in the range $1 \cdot 10^{-7}$ to $3 \cdot 10^{-3}$ m.

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