CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci
 ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124098

Study Of Sorptive Deformation Of Sorbent Using Dilatometric Method

Andrey Tvardovskiy [a*], Vitaliy Nabiulin[a], Anatolii Fomkin[b]

[a] Department of General Physics, Tver State Technical University
Af. Nikitin emb., 22, Tver 170026, Russia, atvard@tversu.ru
[b] Laboratory of Adsorption, Institute of Physical Chemistry and Electrochemistry RAS

Deformations of granulated recuperative activated carbon AR-V (produced in granulated form from coal dust (coals mixture) and adhesion agents by steam treatment at the temperature of 1100 — 1200K) upon carbon tetrachloride adsorption has 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. These results were compared with the adsorption isotherms. 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,1997,1999), (Calle,1988), polymeric materials (Keller et al, 1999), (Zhang et al, 1997), carbons (Bangham,1937), (Haines and McIntoch, 1947), (Wiig and

Please cite this article as: Tvardovskiy A., Nabiulin V.V. and Fomkin A.A, 2011, Studies of sorptive deformation of sorbents using dilatometric method, Chemical Engineering Transactions, 24, 583-588
DOI: 10.3303/CET1124098

Juhola, 1949), (Yakovlev et al, 2003, 2004), (Fomkin et al, 2005) and zeolites (Krasilnikova and Kochirzhik, 1988) 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 sorptive deformation of adsorbent AR-V upon carbon tetrachloride adsorption. To solve this problem, an inductive-type dilatometer was used.

2. Method, Results and Discussion

Deformation of the AR-V microporous carbon adsorbent during adsorption of CCl_4 in the temperature interval from 255.5 to 353 K and at pressures of $1\text{-}14\cdot10^3$ Pa was studied.

The structure-energy characteristics of AR-V adsorbent were determined based on the adsorption isotherm of the standard benzene vapor at 293 K using the computational apparatus of Dubinin's (1947) theory of the volumetric filling of micropores (TVFM) The following characteristics of the adsorbent sample were obtained: micropore volume Wo = 0.26 cm^3/g, characteristic energy of adsorption E_0=15.8kJ/mol, and characteristic micropore half-width x_0 = 0.76 nm.

An inductive-type dilatometer designed for measuring small deformations of solids during adsorption in pressure and temperature ranges of 1-2 x 10^7 Pa and 77-570 K, respectively, was used. The scheme of the dilatometer is shown in Fig. 1: the core (7) of the induction converter (8) of linear displacements is connected with the rod (5) supported on the quartz plate (2), which is placed on the sample (3). The latter is placed inside the ampoule (4) between the quartz disks (2). The ampoule is connected to the dilatometer body through the screw (6). A change in the sample length results in the displacement of the core, which is detected by a digital voltmeter using a transformer. The dilatometer is connected to adsorption installation through a vacuum valve.

During experiments, the temperature in the dilatometer section containing the sample was held constant with an error of ±0.2 K. The rest volume of the dilatometer, along with the induction converter and the adsorption installation, was thermostatted in an air thermostat at 303 K.

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 adsorbent sample in shape and sizes. The dilatometer used allowed measurement of absolute deformations in the range from $1\cdot10^{-7}$ to $3\cdot10^{-3}$ m. Absolute errors of relative linear adsorbent deformation, $\Delta l/l$, if plotted, did not exceed the linear size of the experimental points presented in Fig. 3.

Adsorption of CCl_4 was studied using a gravimetric vacuum adsorption installation with the electronic compensation of the weight change in three intervals with limits of 1, 10, and 100 mg. The error of measurement did not exceed 1 %. The gas pressure was

determined by M10 and Ml000 pressure bellows gauges with measurement intervals of 1-1 · 10^3 and 10-1.5 · 10^5 Pa and errors of ±0.1 and ±1.0 Pa, respectively.

Prior to the measurements, adsorbent AR-V were degassed by heating at corresponding temperatures in vacuum down to a residual pressure of $1{,}33 \cdot 10^{-3}$ Pa in the system. Carbon tetrachloride was thoroughly purified and dried, after CCl_4 was degasses in vacuum, its vapor pressure corresponded to the tabular value.

The isotherms of carbon tetrachloride vapor adsorption on dehydrated AR-V samples (Fig. 2) are S-shaped and characterized by narrow hysteresis loops in the relative pressure range P/Ps= 0.2–0.3. Initial parts of the isotherms are reversible.

The plots of the relative linear deformation of the AR-V carbon adsorbent as function of vapor pressure CCl_4 at temperatures from 255.5 to 353 K are presented in Fig. 3. As follows from the data in Fig. 3, the contraction of the sample achieves a value of 0.68% at 353 K. At higher value of adsorption, the contraction is replaced by expansion. With the temperature decrease the effect of relative expansion increases from 0.17% at 313 K to 0.78 % at 255.5 K.

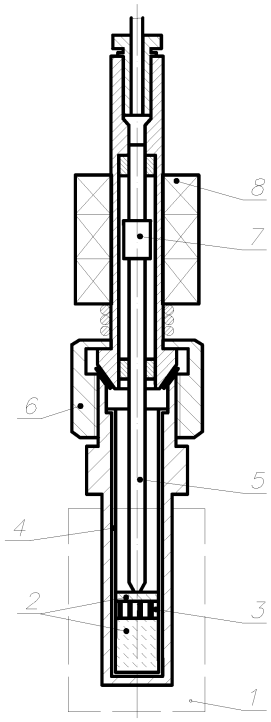

Figure 1: Dilatometric part of the unit; 1, thermostat; 2, quartz polished disks; 3, adsorbent; 4, ampoule with the adsorbent; 5, rod; 6, nut; 7, core; 8, transformer.

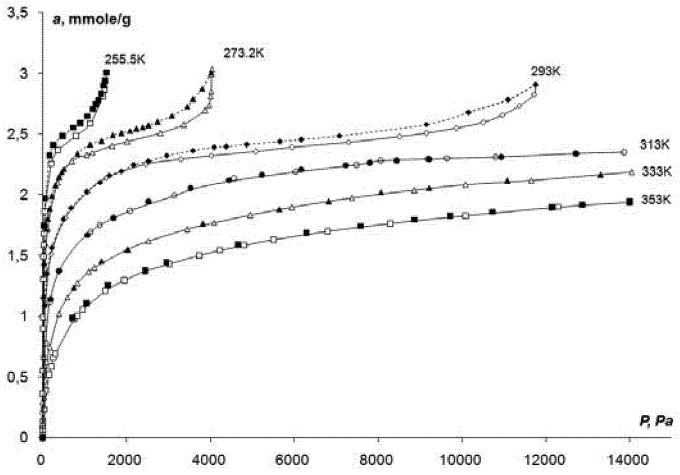

Figure 2: Isotherms of adsorption at different temperatures.

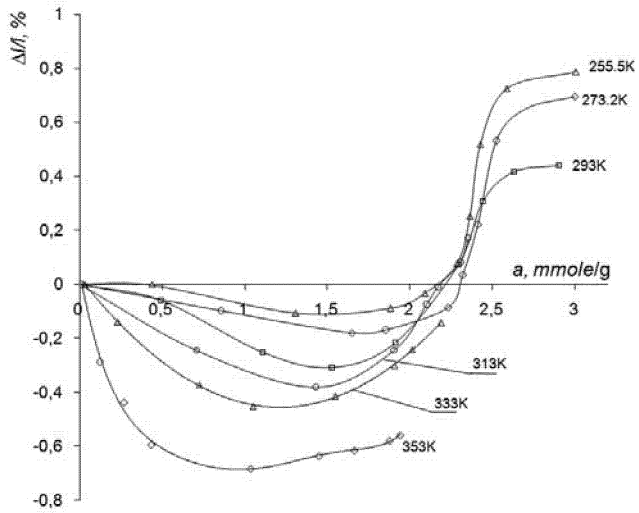

Figure 3: Dependencies of relative linear adsorbent deformation Δl/l on P at different temperatures

3. Conclusion

Deformation of activated carbon adsorbent AR-V upon CCl_4 adsorption has 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. These results were compared with the adsorption isotherms. 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.

References

Bangham D.H., Razouk R.J., 1937, The wetting of charcoal and the nature of the adsorbed phase formed from saturated vapors, Transactions of the Faraday Society , 33, 1463-1472.

Calle C., Suquet H.,1988, Vermiculites.// Rev. Mineralogy, 19. Miner. Soc. America, Washington, 19, 455.

Dubinin, M.M., Adsorbtsiya i poristost' (Adsorption and Porosity), Moscow: VAKhZ, 1971. (in Russian).

Fomkin A.A., 2005, Adsorption of Gases, Vapors and Liquids by Microporous Adsorbents, Adsorption, 11, 425.

Haines R.S., McIntoch R., 1947, Length changes of activated carbon rods by adsorption of vapors, Journal of Chemical Physics, 15, 28.

Keller J.U., Rave H. and Staudt R., 1999, Measurement of gas absorption in a swelling polymeric material by a combined gravimetric-dynamic method, Macromolecular Chemistry and Physics , 200, 2269.

Krasilnikova and M. Kochirzhik, 1988, Study of intracrystalline diffusion by adsorptive deformation method, Russian Chemical Bulletin, 4, 624

Meehan F.T., 1927, The expansion of charcoal on sorption of carbon dioxide,

Proceedings of the Royal Society A, 115, 199.

Tvardovskiy A.V., 2006, Sorbent Deformation. Elsevier, Amsterdam, the Netherlands, 286.

Tvardovskiy A.V., Fomkin A.A., Tarasevich Yu.I. and Zhukova A.I., 1997, Hysteresis Phenomena in the Study of Sorptive Deformation of Sorbents, J. Colloid Interface Sci., 191, 117.

Tvardovskiy A.V., Fomkin A.A., Tarasevich Yu.I. and Zhukova A.I.,1999, Adsorptive Deformation of Organosubstituted Laminar Silicates, Journal of Colloid and Interface Science, 212, 426.

Wiig O.E.. Juhola A.J., 1949, The adsorption of water vapor on activated charcoal, Journal of the American Chemical Society, 74, 561-567.

Yakovlev V.Yu., Fomkin A.A., Tvardovski A.V., 2004, Adsorption and deformation phenomena at interaction of N_2 and microporous carbon adsorbent, Journal of Colloid and Interface Science, 280, 305-308.

Yakovlev V.Yu., Fomkin A.A., Tvardovsi A.V., 2003, Adsorption and deformation phenomena at the interaction of CO_2 and a microporous carbon adsorbent, Journal of Colloid and Interface Science, 268, 33-36.

Zhang Y., Gangwani K.K. and Lemert R.M., 1997, Sorption and swelling of block copolymers in the presence of supercritical fluid carbon dioxide, The Journal of Supercritical Fluids, 11, 115