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ESTIMATION OF SORPTION PARAMETERS OF SOLIDS BY MEANS OF DERIVATOGRAPH Q

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Abstract

Derivatograph Q-1500D was completed with a partial vapour pressure control unit in order to study the sorption phenomena. The proposed arrangement allows to perform time consuming experiments at ambient atmospheric pressure in the temperature range 10–200°C.

Keywords: sorption device, sorption vapours, thermoanalyser Q-1500D

Introduction

Currently common methods for sorption parameters estimation of solid substances are used first of all for physico-chemical characterisation of the solid surfaces. Standardised techniques, e.g. for specific surface estimation or pore size distribution estimation, are available. Despite their common use, the apparatuses developed for these purposes have certain disadvantages, namely limited possibilities at the gaseous sorbate selection as well as doubtful applicability for many practical tasks performed at ambient atmospheric pressure. Estimation of the specific surface of substances with expandable structures, e.g. clay minerals by nitrogen adsorption method, is limited. Values found by this method differ by an order from the real ones, resulted from adsorption of water vapours.

A considerable part of sorption experiments under atmospheric pressure is possible to do on a device designed for thermal analysis. Employment of thermal analysers for such a purpose is justified when the change of sorption capacity of a substance (adsorbed amount) is possible to register as a change of sample mass. This contribution describes technical realisation of such a solution using thermoanalyser Derivatograph Q-1500D. The employment of the old type of device with rather low sensitivity TG detector is compensated by possible use of higher sample mass as well as construction adjustment of the device allowing a technically simple realisation of the suggested solution.

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Experimental

Experiment description

Derivatograph Q-1500D (MOM, Budapest) additionally equipped with the interface for digital output from the electronic mass detector was used in this work [1]. The proposed technical design of the apparatus is in Fig. 1. The sample to be analysed is placed in an aluminium, inside teflon coated crucible with diameter 40 and height 20 with 0.1 mm sheet thickness. The shape of the crucible enables a good contact of the analysed sample with vapours of a liquid. The crucible with the sample is mounted on a ceramic tube with the thermocouple. The contact of vapours with the sample is realised in a double shelled glass vessel placed instead of the heating body of the thermobalance. The temperature of the vessel is controlled by the temperature of the heating jacket filling that circulates in the thermostat number 2. Vapours admission from two saturation columns is in the upper part of the vessel. Two standard Liebig condensers with the total length of 180 cm and inside diameter of 1.5 cm, filled up to

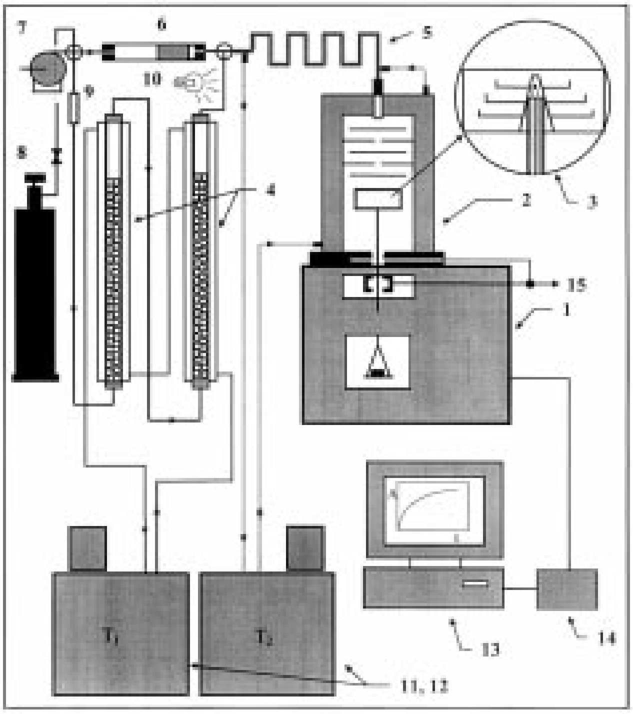

Fig. 1 Diagram of sorption apparatus. 1 – body of thermoanalyser; 2 – double shelled glass vessel; 3 – arrangement and location of the crucible with sample in detail; 4 – saturating columns with a liquid; 5 – heat exchanger; 6 – tube with hygroscopic packing; 7 – air pump; 8 – pressure cylinder; 9 – flow meter; 10 – infrared lamp; 11, 12 – thermostats; 13 – PC; 14 – interface; 15 – connection to vacuum pump

3/4 of its height with glass pellets with 2 mm diameter. The evaporating liquid level height is about 7 cm below the level of the glass packing of the condenser that prevents liquid leaking from the column to the analysed sample. From the same reasons, the second saturating column ends with a simple drop catcher. A heat exchanger is inserted between the column and the vessel with sample. This allows a gradual heating of the vapours flowing from the column outlet to the temperature of analysed sample. Since the positions of the vessel with the sample and both saturating columns, respectively are fixed, the heat exchanger is made as an elastic joint of two poly(ethylene) pipes. The outer one is serially connected with the heating jacket of the vessel above the sample. The required temperature is finally reached by the insertion of barrier series (made of Al-foil) in the upper part of the vessel. The saturated vapours are transported from the columns by flow of air or an air pump through a regulating valve placed on the intake side of the pump. The rate of flow can be adjusted at the recomended value 40 l h^{-1} [2]. Air (or any other carrier gas) with a vapour content is drawn off by a vacuum pump through a circle segment preventing entering of vapours into weighing part of the apparatus. In the case of desorption experiments, the apparatus is adapted by insertion of a tube with desiccant before the heat exchanger. It is made of two separated packings of silica gel and P_2O_5. A conventional arrangement of desorption can be used at temperatures above 200°C, published in [2].

Application possibilities

The arrangement described allows to follow up the kinetics of sorption and/or desorption processes under atmospheric pressure under either isothermic or non-isothermic conditions in the temperature range from 10 to 200°C. The change of the relative vapour pressure above a sorbent, necessary for obtaining sorption isotherm, can be controlled by change of temperature in the column. However, this is possible in the case when the ratio of the sample temperature and the column temperature is greater than 1 (T_2/T_1>1). A simple alternative modification of the sorption apparatus is possi-

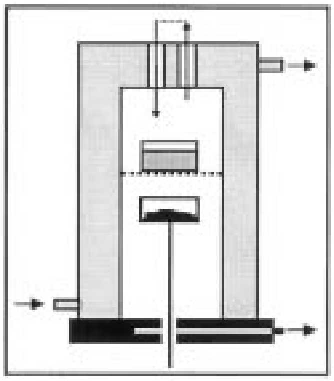

Fig. 2 Proposed arrangement for isothermic sorption, where required partial vapour pressure above a sample is controlled by use of a given concentration of a convenient solution in the dish above the sample

ble to use in the case of such isothermic measurements where the relative vapour pressure can be controlled by concentration of a convenient solution. This is most frequently used when the relative water vapour pressure is to be controlled. In such cases, solutions of sulphuric acid are used as the solutions with defined water vapour pressures. The analysed sample is placed in the heated vessel under a dish with the solution (Fig. 2). The employment of a peristaltic pump can increase the circulation of vapour in a closed circle.

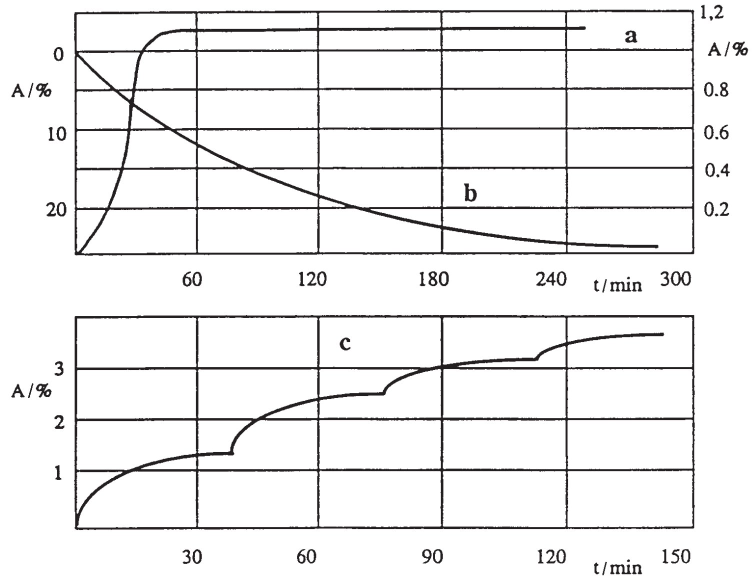

Fig. 3 Mass change of three different samples SiO$_2$-aerogels [2] as a result of a – sorption and b – desorption of water vapours at the temperature 25°C; c – sample mass change under successive increase of relative pressure (p_r= 0.2, 0.4, 0.6, 0.8) (sample temperature: 60°C)

An advantage of proposed arrangements is that the amount of analysed sample can be extremely raised. This proved to be of a great importance in the case of low sorption capacities of low densities of analysed samples, e.g. organic or inorganic porous materials, fine-grained substances with a large apparent volume of powder. An example of sorption and desorption of water vapour on a granulated SiO$_2$-aerogel with density 0.18 g cm^{-3} shows employment of the apparatus (Fig. 3). (Preparation and physico-chemical properties of aerogel is described in detail in [3–5] The employment of the described apparatus proved to be convenient in the case of studying sorption properties of aerogels with densities below 0.1 g cm^{-3}.

Conclusions

Adaptation of thermoanalysers for sorption and/or desorption experiments, that are highly time consuming, appears to be a good possibility to employ old types of devices while some technical weak points of them become an advantage in specified cases.

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