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MAGNETIC SUSPENSION BALANCE FOR SIMULTANEOUS MEASUREMENT OF A SAMPLE AND THE DENSITY OF THE MEASURING FLUID

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Abstract

This paper deals with gravimetric measurements of adsorption equilibria of gases on the surface of porous solids with a new type of magnetic suspension balance. Items discussed include the measurement of adsorption data at high pressure and temperature as well as the simultaneous measurement of adsorption and the density of the adsorptive gas using only one magnetic suspension balance.

Keywords: corrosive gases, density measurement, gravimetric sorption measurement, high pressure and temperature, magnetic suspension balance

Introduction

Gravimetric measurements of adsorption equilibria of gases on the surface of solids are known to be highly accurate, reproducible and to reach a far better resolution than applying the volumetric measuring method. However, as a result of the limited range of applicability in pressure and temperature of the adsorption measuring instruments with microbalances enclosed in the measuring gas, the volumetric based apparatus for adsorption measurement in laboratories are widely used. The above mentioned disadvantages of the gravimetric technique can be eliminated if the high resolution balance and the sample under investigation are physically separated. The sample is exposed to the measuring atmosphere while the balance is located under ambient conditions. This is achieved by using a magnetic suspension coupling, shown in Fig. 1, which transmits the force acting on the sample due to gravity through the wall of a pressure and temperature resistant vessel to the high resolution balance located outside the vessel [1–4].

First, we briefly present a summary of a sorption measuring apparatus with magnetic suspension balance (MSB) for universal use and some examples of its application. Then we give a more detailed report about a newly developed, highly sophisticated type of MSB for the simultaneous measurement of adsorption equilibria and the density of the adsorptive.

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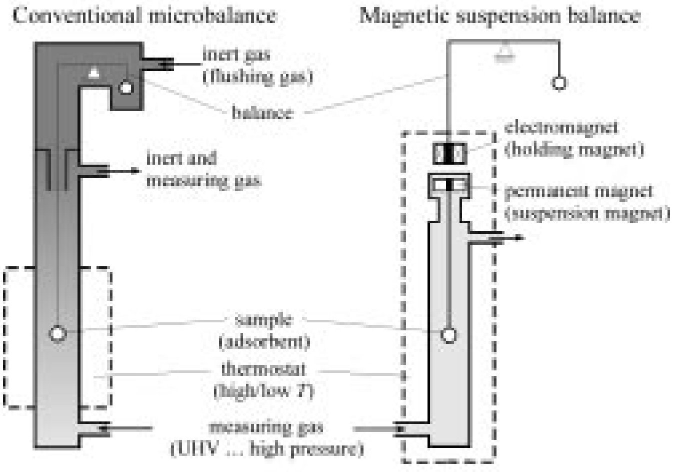

Fig. 1 Gravimetric measurements under controlled environments. Comparison of conventional instrument (left) and magnetic suspension balance (right)

Universal sorption measuring apparatus

The apparatus shown in Fig. 2 allows for sorption measurements to be carried out with almost any pure or mixed gas or liquid in the pressure range from ultra high vacuum to 500 bar at temperatures between 77 and 700 K. High resolution (0.01 mg) gravimetric measurements in this huge range of applicability can be performed by separating the microbalance from the measuring atmosphere by means of a magnetic suspension coupling. This coupling consists of an electromagnet, hanging at the underfloor weighing hook of a microbalance located outside the measuring cell, and a suspension (permanent) magnet inside the measuring cell to which the sample (adsorbent) is connected. The electromagnet voltage is modulated by a controlling unit in such a way that the suspension magnet and the connected sample achieve a constant vertical position in the measuring cell. In this position the magnet and the sample are freely suspended and their mass is transmitted to the microbalance through the wall of the (glass or metal) pressure vessel.

Sorption processes on almost all types of samples (e. g. powders, pellets, liquids, polymers) with masses up to 100 g can be investigated in the above mentioned pressure and temperature range with outstanding reproducibility (±0.015 mg). The so-called measuring load decoupling allows the sample to be set down on a support by varying the vertical position of the permanent magnet by means of the controlling unit. When the sample is set down only the permanent magnet is in suspension and only its mass is transmitted to the balance. In this position the balance can be calibrated and tared. This feature enhances the accuracy of the measurements considerably. The measuring cell and the coupling area are enclosed by thermostats for temperature control of the measuring gas and the sample. Depending on the desired mea-

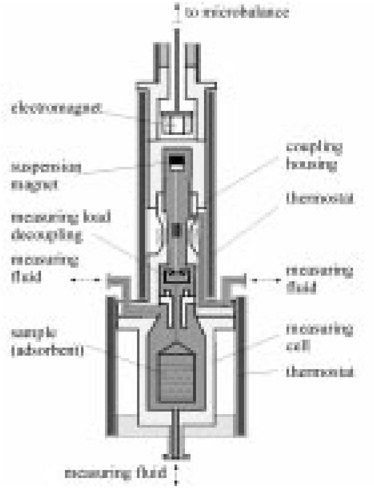

Fig. 2 Universal sorption measuring apparatus with magnetic suspension balance

suring temperature either thermostating fluid (e. g. water, oil, liquid nitrogen) is circulated through double wall tubes (Fig. 2) or an electrical heating is applied and forces its temperature upon the measuring cell and coupling.

Different types of magnetic suspension balance are used for several types of sorption measurements in a wide range of pressure, temperature with a great variety of adsorptives and/or adsorptive mixtures [5–10], such as:

Adsorption of sub- and supercritical gases on highly porous solids.

Absorption and diffusion in polymers.

Solubility of gases and liquids in plastics.

In the following, we describe a newly developed MSB for simultaneous adsorption and density measurements and the results of some measurements using this instrument.

Simultaneous adsorption and density measurement

The newly developed magnetic suspension balance for simultaneous sorption and density measurements enables sorption on samples to be measured in the same range of pressure and temperature with the same accuracy as described above. In addition to this measurement, a titanium or quartz glass sinker with calibrated, constant volume can be weighed in the adsorptive. With this measurement the density of the atmosphere in the measuring cell (pure/mixed gas or liquid) can be determined according to Archimedes' principle. The working principle of the new type of magnetic suspension coupling for the simultaneous measurement of two samples is shown in Fig. 3.

The new magnetic suspension coupling described above has been integrated in a volumetric adsorption measuring system (Fig. 4). By combining the volumetric and the gravimetric method the coadsorption equilibria of binary gas mixtures can be measured without gas analysis [9, 10]. The experimentally measured density of the

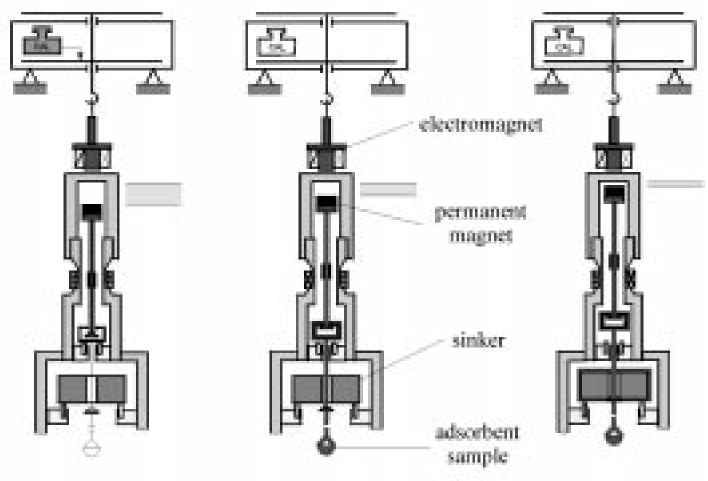

Fig. 3 Simultaneous gravimetric measurements of adsorption on an adsorbent sample and density of the surrounding gas phase with a new type of magnetic suspension balance

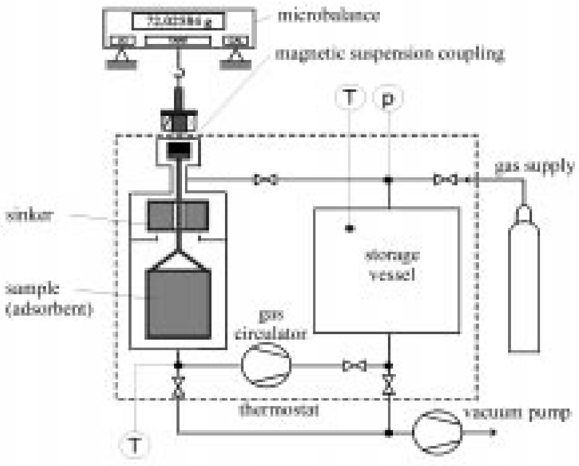

Fig. 4 Schematic drawing of the measuring apparatus for combined volumetric and gravimetric adsorption measurements with magnetic suspension balance

adsorptive is used for the buoyancy correction of the measured adsorption equilibria data and, more importantly for the determination of the concentration of the binary gas mixture in the equilibrium state of the adsorption.

The volumetric measurement is realized using a storage vessel with known volume. In this vessel the desired gas mixture is prepared for adsorption at a certain pressure, temperature and composition. After the preparation, the valves between the storage vessel and the adsorption chamber are opened. In the adsorption chamber the reactivated adsorbent is contained and connected to the balance by means of the magnetic suspension coupling. Supported by the circulation pump the coadsorption equilibrium is achieved and in the equilibrium state the pressure and temperature are measured and, of course, the density of the gas mixture and the mass of adsorbate weighed with the magnetic suspension balance. After the equilibrium data have been measured, the whole system is evacuated and the adsorbent sample reactivated as necessary for the next coadsorption measurements.

The data handling procedure of this combined measurement requires the determination of the concentration of the gas mixture from the measured density, pressure and temperature data. For this, either an accurate equation of state (EOS) for the mixture is needed or calibration measurements for the density of the gas mixture at given concentration, pressure and temperature have to be performed. Once the concentration of the gas mixture is determined the material balances have to be performed for the calculation of the masses adsorbed of the components of the mixture.

During this study the coadsorption equilibria and the densities of the gas mixture CH_4/H_2S were measured on a hydrophobic zeolite DAY at t=25°C in the pressure range from vacuum to 10 bar. We also measured the density/pressure functions at constant temperature for three binary mixtures CH_4/H_2S at given concentrations in calibration experiments. In addition, the adsorption equilibria and the densities of the pure gases CH_4 and H_2S were measured at the same temperature on the same adsorbent in the pressure range up to 20 bar.

Results

The measured densities of the pure gases showed excellent agreement with their values calculated by reference (EOS) available in literature for these gases [11, 12]. Deviations between measured and calculated density values were calculated and found to be far below 1%. These values verify the high accuracy of the density measurement in this combined measuring technique.

The densities of the gas mixture CH_4/H_2S measured during the calibration experiments were compared to their values calculated using the EOS for this mixture [12]. The resulting deviations were surprisingly high (up to 15%), this demonstrates the critical lack of reliable EOS for mixtures and the benefits of a combined density and sorption measurement.

The experimental density values, measured in calibration experiments, were used for the analyzing procedure of the measured coadsorption data: i. e. the calculation of the composition of the gas mixture from the density measurements during coadsorption experiments. In addition to this data analysis we performed the same analysis with the EOS given in the literature and compared the results of both. It transpired, that the deviations between both are up to 25%! The experimental data basis was the same for both, however in one case the densities measured in calibration experiments and in the other case the EOS given in the literature were used. Just using an incorrect EOS for the adsorptive mixture can lead to this misleading results in coadsorption measurements.

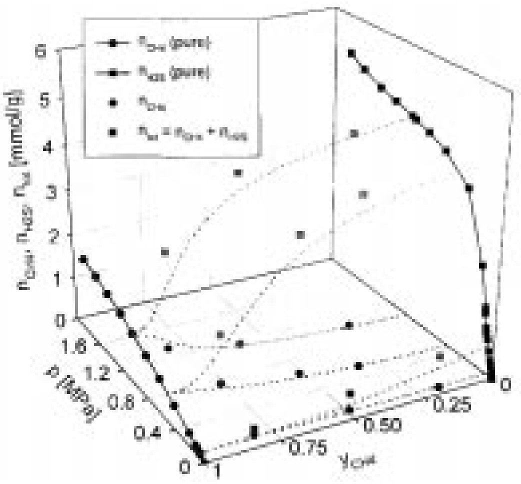

Fig. 5 Adsorption equilibria of the pure gases CH_4 and H_2S and of the mixture CH_4/H_2S on the zeolite DAY at *t*=25°C

The adsorption equilibria of the pure gases CH_4 and H_2S as well as the coadsorption equilibria of the binary mixture CH_4/H_2S on the hydrophobic zeolite DAY measured with the new MSB are shown in Fig. 5 as function of the pressure of the adsorptive (p) and the concentration of methane in the gas phase (y_{CH_4}). The adsorption equilibria shown were determined from the experimental data using the density/pressure functions measured during the calibration experiments. The lines through the pure gas adsorption equilibria in the plot represent a fit with an analytical Langmuir adsorption isotherm, which was chosen due to the Type I adsorption behavior [13] of the measured data. The lines in the mixture area are a pre-calculation of the measured mixed gas adsorption equilibria using the Langmuir isotherm with parameters determined by the fit of the pure gas data.

Conclusions

Magnetic suspension balances allow gravimetric sorption measurements to be performed in a range of pressure and temperature using adsorptives inaccessible for almost all other (gravimetric and/or volumetric) instruments. The great range of applicability in pressure and temperature as well as the variety of useable adsorptives (among others: corrosive gases) distinguish the magnetic suspension balance from all other commercially available adsorption measuring apparatus. Using these magnetic suspension balances various types of sorption measurements are performed in academia and industry.

The new type of magnetic suspension balance permits the simultaneous gravimetric measurement of adsorption equilibria of pure gases or gas mixtures and of the density of the gas or the gas mixture. The simultaneous density measurement has proved to be not only advantageous but absolutely necessary for all adsorption equilibria measurements using adsorptives for which the thermal equation of state is not precisely known. It was demonstrated, that density values calculated for the gaseous mixture CH_4/H_2S with the EOS, which is assumed to be the best one for this mixture, differed from the measured values by up to 15%!

Adsorption and coadsorption data analyzed with this incorrect EOS differed from their values determined using the measured, true density values, by up to 25%. This demonstrates clearly the advantages of using the simultaneous density and adsorption measuring apparatus.

Simultaneous density and adsorption measurement should be applied in general:

At high pressure (density) sorption measurements.

Using adsorptives with unknown or inappropriate equations of state.

When working with mixed adsorptives.

The applicability of the new technique has been clearly demonstrated and its benefits for the determination of the adsorption equilibria of pure gases and gas mixtures proven.

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