Gas Storage Capacity of MOF Materials - Measuring High Pressure Methane Adsorption

Keywords: Gas storage, High Pressure Adsorption, Methane, Hydrogen, MOF, Gravimetric Measurement TA396

ABSTRACT

The high storage capacity of porous MOF materials for adsorbed gas is discussed as a promising method for utilizing natural gas or hydrogen as fuel for mobile applications. Currently the development of new porous MOF materials with high natural gas storage capacity is a vital area of research. Accurately measured gas adsorption data are the basis for evaluation and comparison of the natural gas storage potential of new and classical MOF materials. Gravimetric measurements of gas adsorption equilibrium data and kinetics with magnetic suspension balance instruments by TA Instruments provide highly accurate results in a large pressure range.

INTRODUCTION

Natural gas, as methane (CH4), has a considerable advantage over conventional fossil fuels for mobile applications both from an environmental point of view as well due to the natural abundance and resources. The storage of adsorbed natural gas in porous materials, eg. the storage capacity of methane, is discussed as a promising method for utilizing natural gas as fuel with sufficiently high energy density. Thus, the development of new porous materials and measuring their storage capacity for methane at high pressures is a vital area of research.

MATERIALS

A material for adsorptive gas storage should have a high specific surface area - so porous materials are the most promising candidates. A key factor for the interaction of methane with the material is the size of the pores. Numerical simulations have shown that the maximum storage capacity of methane is attained within pores of 1.1 nm in diameter.

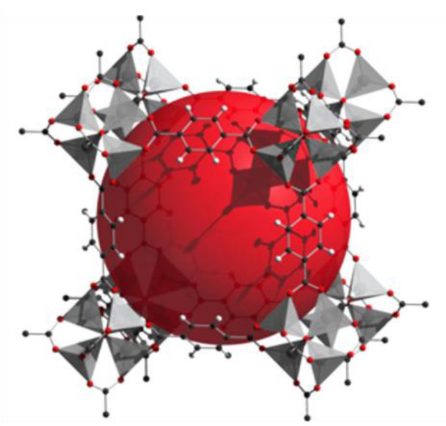

Figure 1: IRMOF-1, a Zn-based MOF material with pores of 1.4 nm and 0.9 nm.

A new group of porous materials was developed from the mid 90's, the so called metal-organic frameworks – MOF materials - or coordination polymers. Such MOF materials consist of metal atoms or metal/oxygen-clusters, which are connected by organic linkers.

By choosing the linkers and also metal-clusters hundreds of different porous materials with large specific surface areas and well-defined pore sizes in the nm-range can be synthesized.

EXPERIMENTAL EVALUATION OF THE STORAGE CAPACITY OF MOF MATERIALS

A gravimetric sensor is the most accurate high pressure adsorption measuring device. Gravimetric measuring instruments equipped with magnetic suspension balances are widely applied in gas storage research, as in research for gravimetric adsorption measurements, and related material sciences, i.e. MOF materials. TA Instruments offers various high pressure versions of gravimetric adsorption measurement analyzers (up to 150 bar, 350 bar or even 700 bar).

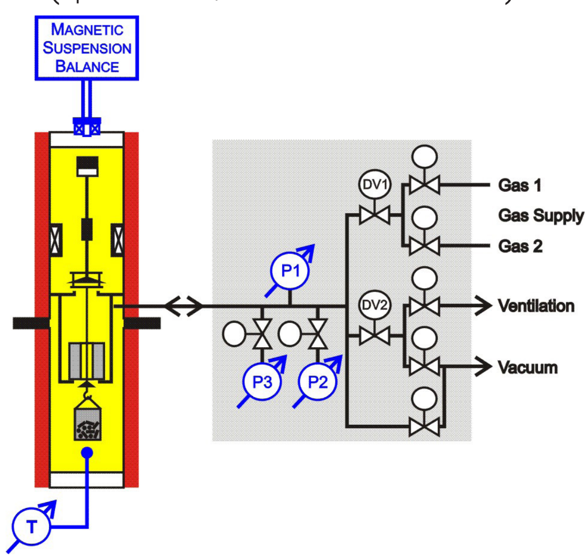

Figure 2: Flow diagram of gravimetric high pressure adsorption analyzer with magnetic suspension balance.

Using the magnetic suspension balance instruments the sorption measurement, ad- or desorption equilibrium data as well as the kinetics of adsorption can be measured in the range from vacuum to the given maximum pressure in a wide temperature range (77 K up to 420 K, depending on chosen thermostat). Activation of the sample material, i.e. MOF material in vacuum at temperatures up to 670 K is monitored in situ and the weight loss of the sample due to the activation procedure is considered in the data treatment.

RESULTS

In Figure 3 the sorption measurement, ad- and desorption equilibrium data of methane (CH_4) on three different MOF materials are presented. The isotherms were measured at 303 K in the pressure range from vacuum to 200 bar [1]. The $Cu_3(btc)_2$ material shows the highest adsorption capacity for methane (CH_4) amongst the three MOF materials. No hysteresis between ad- and desorption branch of the isotherms is present. The highest excess adsorption – i.e. highest storage gain due to adsorption compared to the compressed gas phase – is found as the maximum in the shown isotherms at pressures between 75 bar and 120 bar.

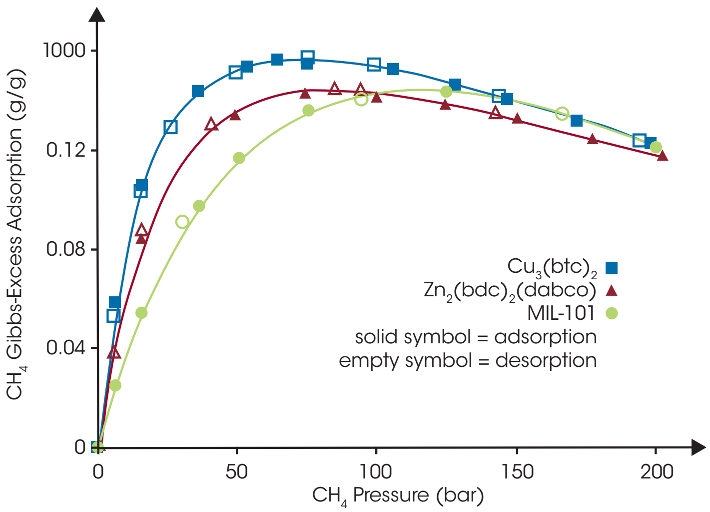

Figure 3: Ad- and desorption isotherm data of CH_4 on three different MOF materials at 303 K [1].

The kinetics of adsorption – i.e. the time needed after changing the pressure until the equilibrium is reached – is recorded by the magnetic suspension balance additionally. From this so-called uptake curves information about kinetic parameters (diffusion coefficients) can be extracted. In figure 4 the uptake curves of four different gases on a SIFSIX-3-Zn-MOF are presented as gravimetric adsorption as function of time [2].

CONCLUSION

Measuring the storage capacity of MOF materials with gravimetric analyzers results in valuable informations about the quality of the MOF material. Adsorption of gases on porous MOF materials may increase the energy density of gaseous fuels in storage tanks for mobile applications.

Newly synthesized porous materials like MOF can be evaluated for their storage potential by measuring the adsorption equilibrium and kinetic data of the potential fuel gases (CH_4, H_2, …).

Magnetic suspension balance instruments allow performing these measurements in a wide temperature and pressure range with highest resolution and accuracy.

The results shown in this application note were measured by our customers using the ISOSORP® SA (400-150 S-G) instrument.

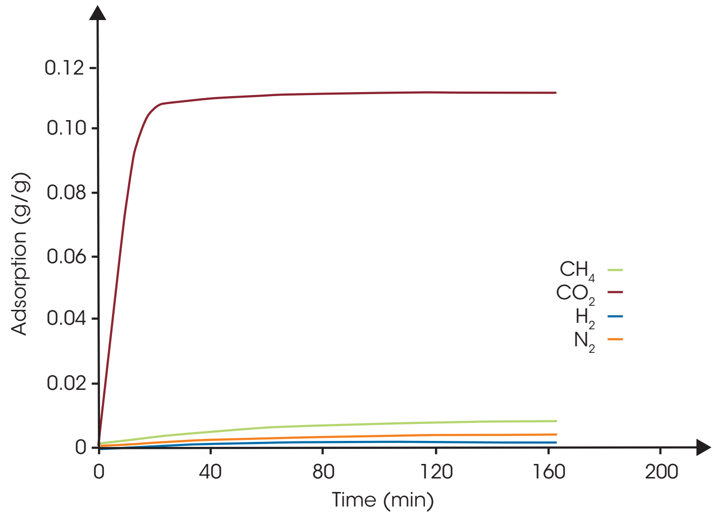

Figure 4: Gravimetric uptake curves of CH4, CO2, H2 and N2 on SIFSIX-3-Zn MOF [2].

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