Measuring H_2, CH_4 and SO_2 sorption by porous materials using the XEMIS microbalance

Isochema Laboratory, Hiden Isochema Ltd, 422 Europa Blvd, Warrington, WA5 7TS, UK

Introduction

High pressure adsorption is of significant interest for a range of applications, including the storage of gases such as hydrogen and methane and the separation and purification of various gas and vapor species. In each case, it is important to be able to accurately characterize the adsorption behavior of different materials under practical conditions; however, measurements at elevated pressures, in particular, can be challenging [1]. Furthermore, the compatibility of components for use with corrosive species, which are of interest for environmental applications, for example, is a serious practical issue.

In this application note, we present data measured under a range of challenging experimental conditions using a Hiden Isochema XEMIS microbalance. For this purpose, we selected a metal-organic framework (MOF), a shale and a zeolite. Of particular note is, firstly, the practical requirement to be able to characterize small MOF samples for research purposes and, secondly, the low gas uptakes shown by shales, which are highly heterogeneous natural materials. Shales are of great practical interest due to the shale gas boom but their characterization requires high pressures and elevated temperatures to mimic geologically-relevant conditions [2].

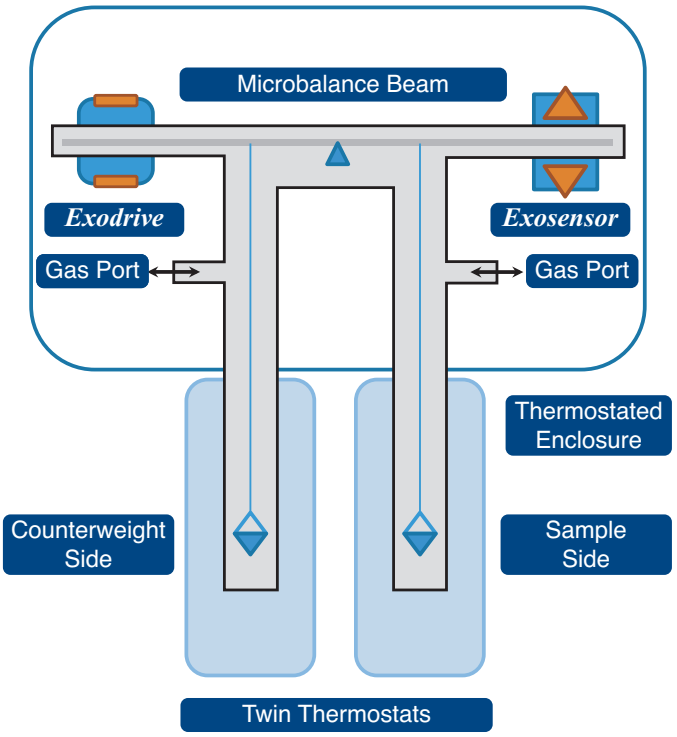


Figure 1: XEMIS microbalance schematic

Experimental Details

The XEMIS is a symmetrical microbalance with the beam position controlled, and sample weight measured, by a novel proprietary feedback system. Sensitive measuring components are located outside the chamber and operation with corrosive species and at high pressures is possible. The microbalance has a maximum capacity of 5 g, a weighing range of 200 mg, a resolution of 0.2 μg and a long term stability of ± 5 μg. The XEMIS operates to 200 bar and 770 K; operation is automated with pressure, temperature and weight readings constantly recorded at intervals from 0.1 seconds, allowing full analysis of the sorption kinetics as well as the equilibrium uptake. A schematic is shown in Figure 1, note not all components are shown.

Results and Discussion

Figure 2 shows SO_2 adsorption-desorption isotherms on a novel MOF, NOTT-300 [3], at five temperatures, each 12.5 K

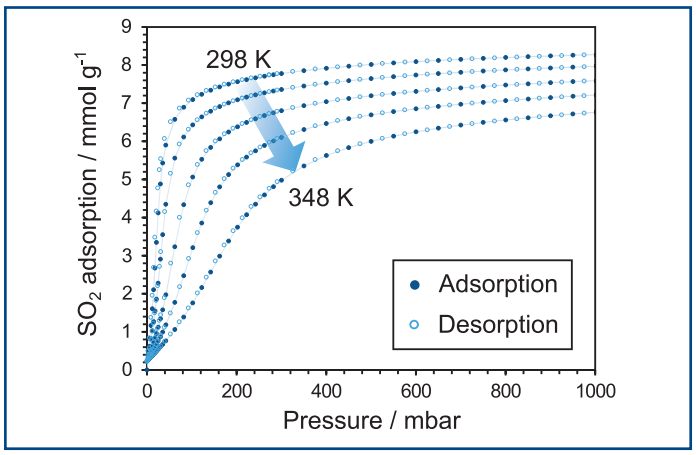


Figure 2: SO_2 adsorption on NOTT-300 (data courtesy of University of Nottingham)

apart in the range 298 - 348 K. It can be seen that the isotherms exhibit excellent reversibility, demonstrating both the excellent long term stability of the XEMIS microbalance and its compatibility with corrosive species. Note the pressure resolution on the x-axis, with pressure setpoints controlled from 3 mbar upwards. For each measurement, the sample was loaded onto the microbalance and degassed for several hours at an appropriate temperature. The temperature of the sample was regulated while gas was sequentially dosed at increasing pressure for the adsorption measurements and decreasing pressures for desorption; the gas pressure being constantly regulated in all cases using a Hiden Isochema XCS gas delivery system integrated with the XEMIS. Figure 3 shows CH_4 adsorption isotherms on alum shale, at five temperatures, each 15 K apart in the range 298 - 358 K. Pressures up to 100 bar are studied and it can be seen that the data are of high quality, given the µmol g^{-1} scale on the y-axis, demonstrating the ability of the XEMIS to perform measurements with samples exhibiting extremely low uptakes. The trend and even spacing of the isotherm is as expected for physisorption, with lower uptakes recorded at higher temperatures. Figure 4 shows H_2 adsorption-desorption isotherms at 77 K measured on a 50 mg sample of Na-X zeolite, at pressures up to 150 bar. The data show good reversibility, as expected for physisorption, and the excess adsorption can be seen to reach a peak around 20 bar before decreasing as the pressure increases

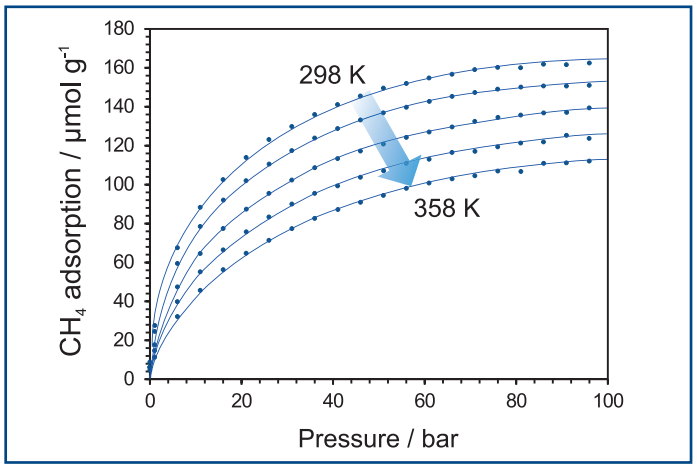


Figure 3: CH_4 adsorption on alum shale

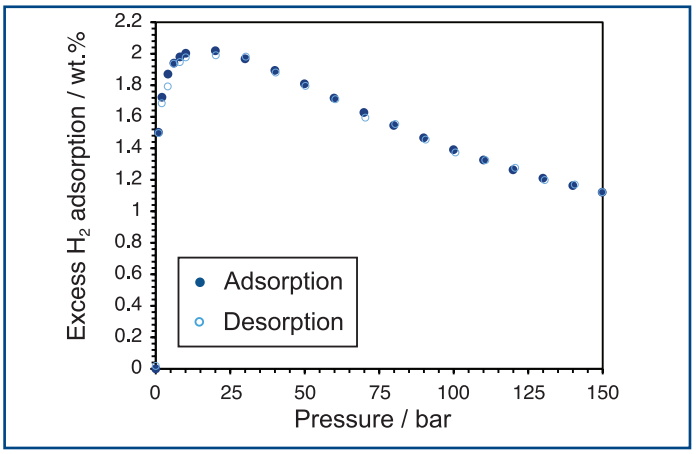
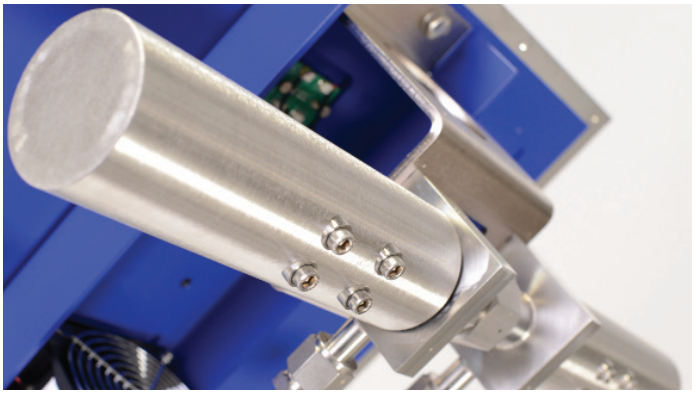


Figure 4: H_2 adsorption on Na-X zeolite at 77 K



further. The behavior is typical for high pressure adsorption under these conditions [1].

Conclusion

In this application note, we have demonstrated the measurement of the adsorption and desorption of H_2, CH_4 and SO_2 using the Hiden Isochema XEMIS microbalance. The XEMIS uniquely allows simultaneous determination of equilibrium uptake and kinetic data using Hiden Isochema's IGA method.

This study has demonstrated the excellent long term stability of XEMIS, making it ideal for measuring low uptakes or investigating research scale sample sizes. The high quality data presented here demonstrates sorption measurements in extreme environments including corrosive atmospheres, at high pressures and temperatures.

References

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