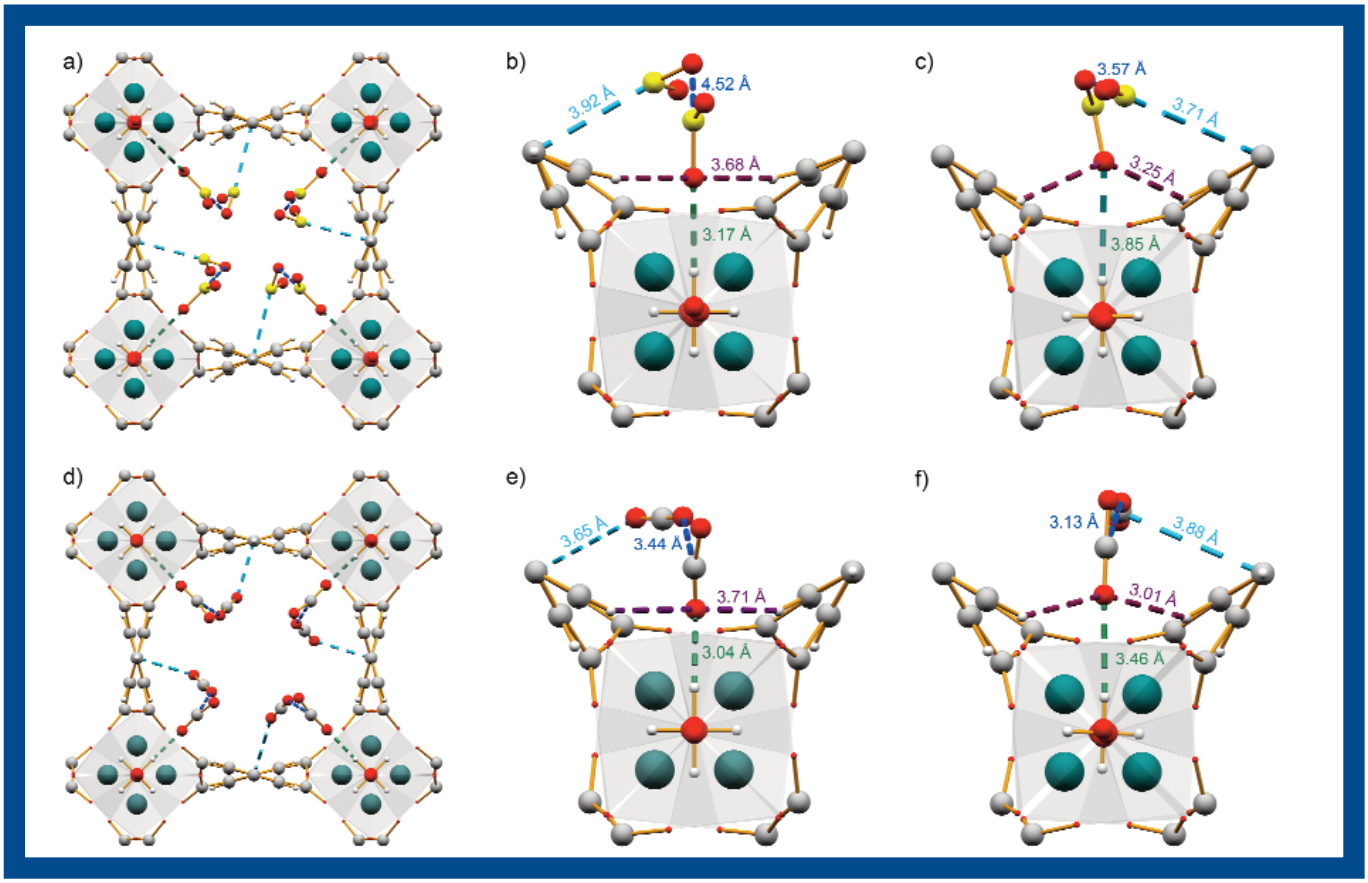
Hiden Isochema
Advancing Sorption Analysis

Newsletter • Autumn/Winter 2016

Unique Features of XEMIS Sorption Analyzers Demonstrated in New Publications

Ever since we installed the first XEMIS gravimetric sorption analyzer, nearly two years ago, our customers have been using this instrument to measure high quality adsorption/desorption isotherms, and a number of publications have now appeared in the literature [1-7]. In this edition of our newsletter, we report on some recent papers demonstrating the unique features of these systems.

Atmospheric pollutant removal with a functionalized MOF



Reproduced from [1] with permission from John Wiley and Sons.

Dr Sihai Yang and Prof. Martin Schröder from the University of Manchester, UK, and their collaborators, including Hiden Isochema scientists, reported selective adsorption of SO_2 by a metal-organic framework (MOF), MFM-300(In), in a paper published in *Advanced Materials* [1]. This material is a functionalized, robust indium and carboxylate-based MOF and shows potential for removing harmful SO_2 from flue gas. It exhibits both a high adsorption capacity and selectivity for SO_2 over other flue gas components such as N_2 and CO_2.

SO_2, N_2 and CO_2 isotherms were measured on samples weighing less than 100 mg. A XEMIS was used for SO_2 and N_2, while an IGA-003 was used for CO_2. High resolution SO_2 adsorption/desorption isotherms had pressure points programmed in 3 mbar increments at the

FS 535721 PART OF THE HIDEN GROUP

422 Europa Boulevard, Warrington WA5 7TS England
t: +44 (0)1925 244 678 e: info@hidenisochema.com
www.hidenisochema.com

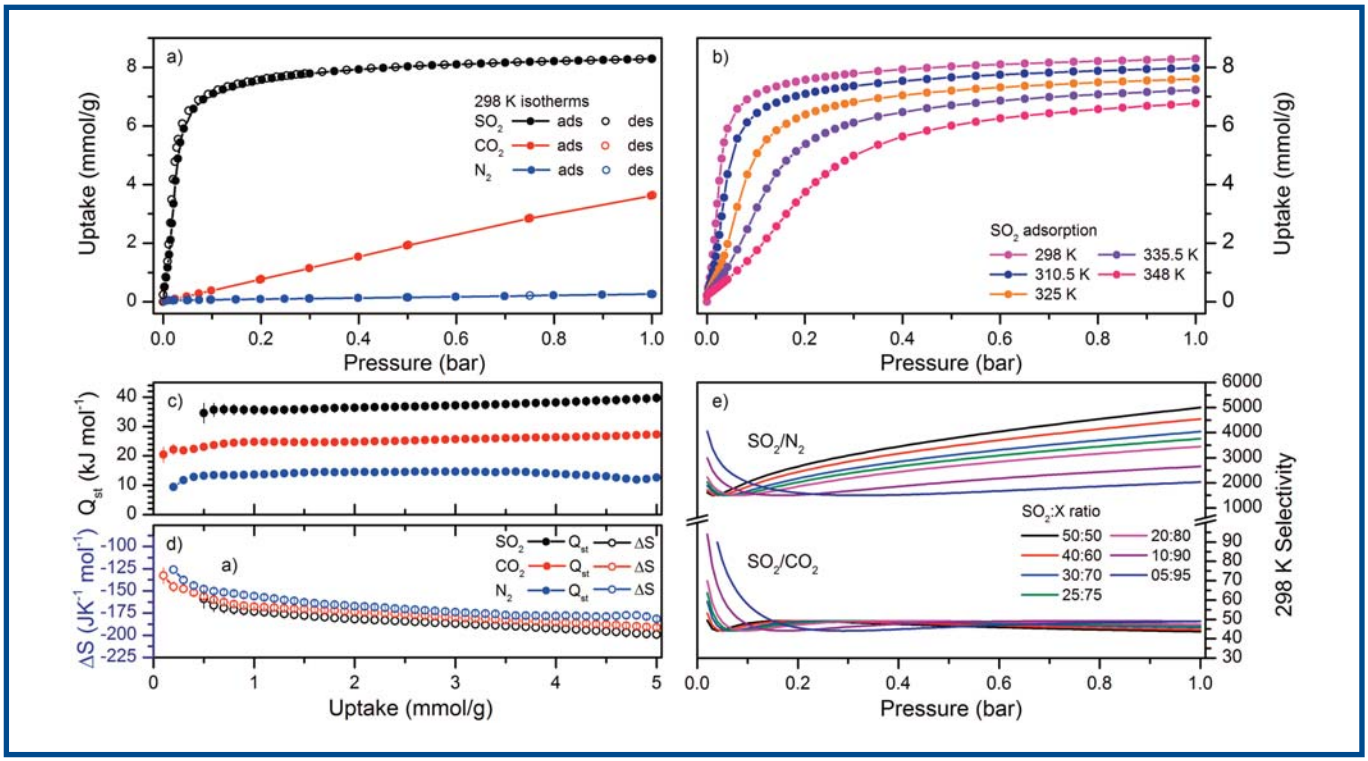


Fig 1. a) N_2, CO_2 and SO_2 adsorption isotherms on MFM-300(In) at 298 K to 1 bar; b) SO_2 adsorption isotherms on MFM-300(in) at 5 temperatures between 298 and 348 K; c) and d) isosteric enthalpy and entropy of adsorption values determined from the adsorption isotherms and e) IAST selectivity of mixtures derived from the isotherms at 298 K for pressures to 1 bar. Figure reproduced from [1] with permission from John Wiley and Sons.

lowest pressures, while N_2 adsorption-desorption isotherms were determined to a maximum pressure of 180 bar. The data were used to determine isosteric enthalpies and entropies of adsorption in the coverage range 0.5 to 5 mmol g^{-1} for N_2, SO_2 and CO_2.

Although pressures of interest for pollutant removal from flue gas are close to ambient, the ability of the XEMIS to measure accurate adsorption isotherms to pressures above 150 bar was required to reach the highest N_2 coverages. High pressure N_2 adsorption isotherms were also important for applying the Ideal Adsorbed Solution Theory (IAST) to SO_2/N_2 mixtures because high coverage data for all adsorbates were then available for the calculations.

Energy gas storage by sustainable carbons and a MOF

CH_4 and H_2 adsorption by the same MOF, MFM-300(In), was reported in another study published earlier this year in the *Journal of the American Chemical Society* [2]. Isotherms were measured on 50 mg samples at different temperatures, and the enthalpies and entropies determined as a function of coverage.

A XEMIS was used for CH_4 adsorption up to 50 bar and an IGA-003 for H_2 adsorption up to 20 bar. Adsorption data were then combined with neutron powder diffraction and inelastic neutron scattering measurements, and density functional theory (DFT) calculations, to determine the location, binding and rotational modes of the adsorbed CH_4 and H_2 molecules.

Meanwhile, a study published in *ACS Sustainable Chemistry & Engineering* [3], co-authored by scientists at the Spanish National Institute of Carbon (INCAR-CSIC, Oviedo) and the University of Nottingham, UK, reported synthesis of high surface area carbons derived from biomass. These sustainably synthesised materials exhibit tailored bimodal porosity, which results in high, controllable gas storage capacities.

Gas separation by novel polymers of intrinsic microporosity

Prof. Tai-Shung Chung at the National University of Singapore and his team recently reported the synthesis, processing and characterization of novel polymers of intrinsic microporosity (PIMs), in a paper published in the *Journal of Membrane Science* [4]. The PIMs incorporate Tröger's base and were cast into films.

A XEMIS sorption analyzer was used to determine the solubility of H_2, N_2, CO_2 and CH_4 in the PIMs. Only 50-60 mg of sample was required in each case. Together with permeation measurements, the data were used to evaluate the gas separation properties of the polymers. The best performing material exceeded the 2008 upper bound of the Robeson plot for H_2/CH_4 separation.

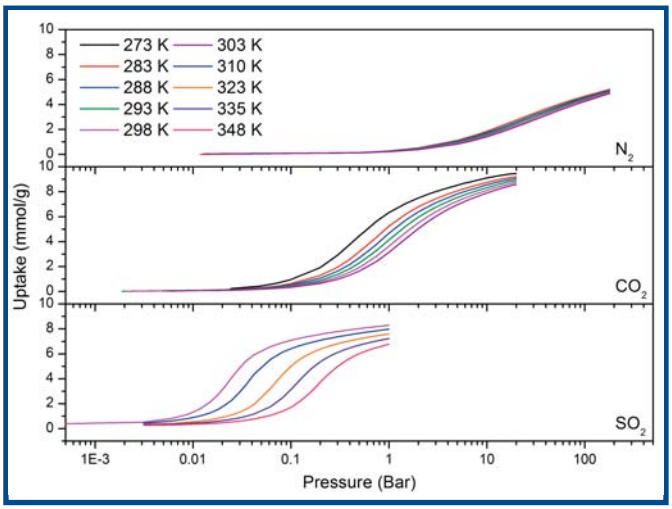
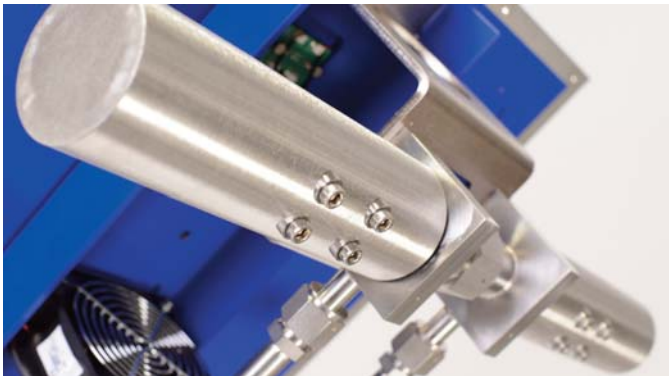


Fig 2. N_2, CO_2 and SO_2 adsorption isotherms on MFM-300(In) in the temperature range 273 – 348 K and at pressures to 180 bar plotted on a logarithmic scale. Figure reproduced from [1] with permission from John Wiley and Sons.

The same group recently reported synthesis and characterization of PIMs modified with β-cyclodextrin (β-CD) [5]. The polymers were prepared in solution and cast by controlled evaporation. Polymers with β-CD contents ranging from 0.1% to 2.0% were prepared, together with a pure material for reference. O_2, N_2, CH_4 and CO_2 sorption was measured at 35 °C using a XEMIS sorption analyzer, with sample sizes again in the range 50-60 mg. For all gases, solubility and diffusivity was found to increase with increasing β-CD content, which can attributed to enhanced microporosity. The combined permeability and selectivity of the β-CD-PIMs also exceeded the 2008 upper bound of the respective Robeson plots for nearly all the materials and combinations of gases studied.

IGA and XEMIS gas sorption analyzers were used for high pressure H_2 and CO_2 adsorption measurements on five different carbons. CO_2 adsorption measurements up to 40 bar, using the XEMIS, illustrated the different CO_2 uptake trends for the carbons studied, which depended on their different bimodal pore size distributions. Mixed micro- and mesoporous materials had consistently higher gas storage capacities at high pressures, compared to those containing mainly micropores. They also possessed enhanced working capacities in a typical pressure swing adsorption (PSA) cycle.



Conclusion

The studies described here, together with those reported previously [6,7], provide an excellent demonstration of the sorption measurements that can be performed with XEMIS gravimetric sorption analyzers. Measurements with H_2, He, CH_4, N_2, O_2, CO_2 and SO_2, from vacuum to 180 bar, with pressure increments as low as 3 mbar, have now been published.

For further details on the range of options for XEMIS sorption analyzers, please contact your local Hiden Isochema representative, or email us at info@hidenisochema.com.

References

[1] M. Savage et al (2016) *Advanced Materials* 28(39), 8705-8711

[2] M. Savage et al (2016) *Journal of the American Chemical Society* 138(29), 9119-9127

[3] M. Sevilla et al (2016) *ACS Sustainable Chemistry & Engineering* 4(9), 4710–4716

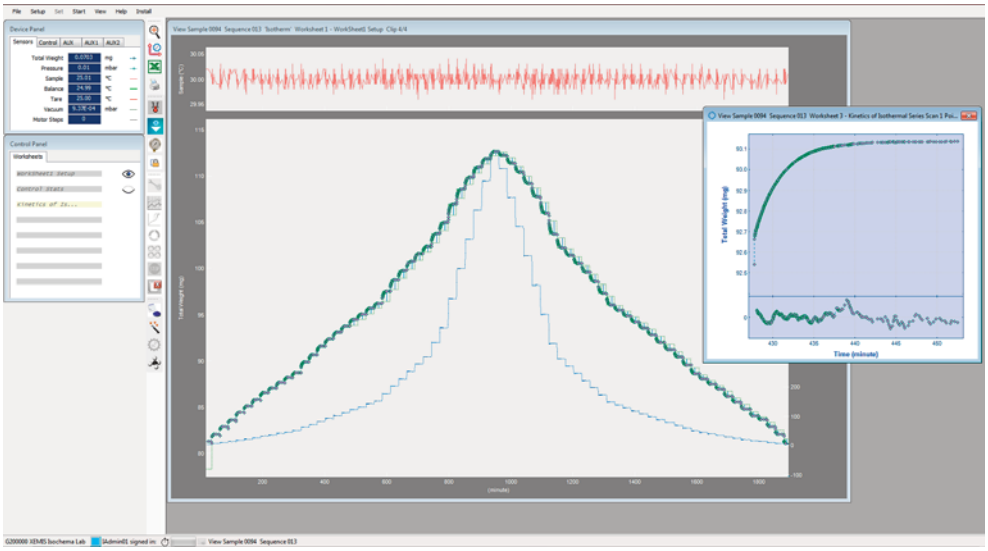
[4] Y. Xiao et al (2017) *Journal of Membrane Science* 521, 65–72

[5] J. Liu et al (2017) *Journal of Membrane Science* DOI: 10.1016/j.memsci.2016.10.001

[6] B. Adeniran and R. Mokaya (2015) *Journal of Materials Chemistry* A 3, 5148-5161.

[7] B. Adeniran and R. Mokaya (2015) *Nano Energy* 16, 173-185

Have you considered migrating to HIsorp?



Customers running Hiden Isochema instruments under legacy software are reminded that Hiden Isochema offer migration to our state-of-the-art platform, HIsorp. HIsorp features a completely modernised user interface, and offers many new features, including improved real time processor functions, all new high resolution graphics with user-specific display options and an integrated, customisable PDF report generator.

For more details please contact your usual Hiden Isochema technical contact or email our Service Department at iservice@hidenisochema.com.

Conference and Exhibition Plans

It has been a very busy conference and exhibition season for us, and we were delighted to have the opportunity to meet so many friends, both old and new, at meetings this year. As we make plans for our 2017 conference and exhibition programme, we will be very pleased to receive your suggestions for meetings that you think a Hiden Isochema presence would be appropriate. Of particular interest are meetings in application areas new to us!

Follow us on Twitter!

@HidenIsochema are on Twitter, and are tweeting about company, research and conference news and anything else scientific that we find interesting!