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In situ studies of gas sorption in porous networks

A. Plonka[1], D. Banerjee[2], W. Woerner[1], J. Parise[1,2]

[1]Stony Brook University, Department of Geosciences, Stony Brook, NY, USA, [2]Stony Brook University, Department of Chemistry, Stony Brook, NY, USA

Selective gas separation is one of the key properties exploited in industrial processes utilizing porous materials. The crystal structure of the native and activated frameworks, along with those of ion exchanged and otherwise modified variants, provide the basis for rational development of gas-selective nanoporous solids. In situ scattering studies of gas-loaded materials provide an understanding of the nature of interactions between sorbed gas and pore surface, which can be vital to development of reliable interatomic potentials, used simulating adsorption behavior. We find that simultaneous observation of the Differential Scanning Calorimetry coupled with x-ray diffraction (DSC-XRD) measurements is a particularly powerful tool 1, 2. The powder diffraction pattern can be monitored for changes, such as framework collapse, as porous materials are heated and activated. Apart from monitoring structural changes, thermal responses accompanying dynamic exposure to gases at variable humidity, and as the temperature is varied, provides a reliable tool in order to screen for new and potentially selective porous materials. The DSC signal provides a reliable means to determine the enthalpy of interaction between framework and gas, and there is experimental evidence this signal may distinguish between gas interactions with bare metal sites in the activated framework and other gas-framework interactions. Studies where the enthalpy of interaction and X-ray scattering from low angle peaks, which are most sensitive to the filling and evacuation of pores of the porous materials are monitored, can be coupled with varying the nature of the gas and the relative humidity. These studies are conveniently carried out with a modified gas manifold interfaced to a slightly modified Rigaku corporation DSC-XRD, which allows studies from about 150 – 600 K. Illustrative examples of the use of this laboratory based equipment, which provide the underpinnings of detailed single crystal studies of gas-loaded materials, include studies of porous calcium based coordination network (CaSDB, SDB: 4,4' - sulfonyldibenzoate), which is selective for CO2, even in the presence of high relative humidity (RH). Recent results from a series of materials studied in the home laboratory and at synchrotron sources will be presented.

[1] *Plonka, A. M.; Banerjee, D.; Woerner, W. R.; Zhang, Z. J.; Nijem, N.; Chabal, Y. J.; Li, J.; Parise, J. B., Mechanism of Carbon Dioxide Adsorption in a Highly Selective Coordination Network Supported by Direct Structural Evidence, Angew. Chem.-Int. Edit.,* ***[2]*** *Plonka, A. M.; Banerjee, D.; Woerner, W. R.; Zhang, Z.; Li, J.; Parise, J. B., Effect of ligand geometry on selective gas-adsorption: the case of a microporous cadmium metal organic framework with a V-shaped linker, Chem. Commun. 2013, DOI: 10.1039/C3CC43*

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