Real time observation of gas-induced structural changes on nanoporous solids

PROPOSAL CODE 25-01-942

22-28 October 2014

Summary and Objectives

The objective of this proposal was to continue the research initiated in previous projects (25-02-774 and 25-01-888) for exploring the gas adsorption/desorption induced transitions phases of a given nanoporous material (ZIF-8) at cryogenic temperatures.

For this purpose a designed cell was used which was constructed in collaboration with the Spline at ESRF in previous projects. The measurement cell allowed the fine control of the gas dosage, sample outgassing in vacuum, temperature control and simultaneous HRPD recording. The pressure and temperature of the sample were controlled from 0-3 to 600 torr and 85 K, respectively.

Data revealed structure deformation by the adsorption of N_2, Ar and O_2 gases, demonstrating that this set-up is perfectly suitable for direct structural analysis at *in operando* conditions. Therefore, the presented results prove the feasibility of this novel experimental station for the characterization at real time of solid-gas reactions and other solid gas processes by SR-HRPD.

Results

The high research interest in crystalline nanoporous materials is boosted by the industrial and environmental applications of molecular separation, gas storage and selective heterogeneous catalysis. Porous coordination polymer networks (PCPs) have emerged as a new class of porous materials with improved properties compared to classical species (i.e zeolites, carbon adsorbents and oxides). A small group of such nanoporous materials have revealed rather unique structural flexibility not commonly associated with crystalline solids. Adsorption and diffusion of gas probes with kinetic diameters larger than the dimensions of the pore aperture of the solid have confirmed the flexibility in these structures. In this context, our previous works on ZIF-8 combining high resolution adsorption/desorption isotherms and molecular simulations have shown that this material has a bi-stable behavior controlled by the gas pressure as external stimulus, which leads to an outstanding structural transformation. Data revealed that the host flexibility seemed controlled by the packing arrangement of the gas inside the pores, and the polarizability and molecular size and shape of the gases.

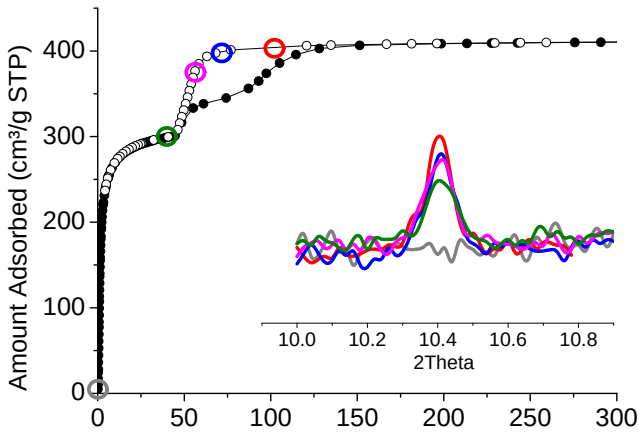

Figure 1: Equilibrium N_2 adsorption/desorption isotherm 85 K of ZIF-8 and (inset) real time HRPD during gas release (desorption).

To clarify the role of the gas probe and/or the gas-framework interactions, and taking advantage of the measurement cell designed and constructed at ESRF we have performed *in-situ* measurements of the X-ray diffraction patterns of this material upon controlled gas adsorption/desorption at cryogenic temperature. For this, we have expanded the study of the phase transitions detected for ZIF-8 to other gases and pressures.

In our experiments, diffraction patterns of ZIF-8 sample were acquired at different gas pressures, 5 points of gas uptake

(adsorption) and another 5 points of gas release (desorption) to cover the full pattern, keeping isobaric and isotherm working conditions during data acquisition. We have used three gases (N_2, Ar and O_2) and a temperature of 85 K. Figure 1 (inset) shows the diffractograms corresponding to nitrogen desorption at 85K at different gas loadings from atmospheric pressure to vacuum following the desorption branch of the isotherm. The spectrum of the sample measured at high vacuum corresponds to the diffraction pattern of ZIF-8 before the gas-induced transition. Then, the reaction gas was dosed into sample at a saturation pressure (fig. 1) and it was decreased until preselected fixed pressures to see the effect of gas desorption on the diffraction patterns. The SR-HRPD were measured in a 2θ range from 3° to 63° corresponding to a resolution better than 0.7 Å.

Outstanding differences were noticed in the patterns, with the appearance of a new diffraction peak when N_2, Ar or O_2 were dosed. The intensity of this peak decreased with the gas pressure, and correlate with the gas desorption features measured in the equilibrium desorption isotherms in a volumetric static apparatus. The study of this kind of ZIF-8 systems and the mechanisms involved in the transitions produced by the gas adsorption/desorption will require further work in the analysis of the presented results. However, the real time monitoring of the HRPD patterns of the material indicate that the gas-induced structural flexibility is linked to the organization of the adsorbed gas molecules in the different adsorption sites of the material. Such direct *in-situ* evidences of structure deformation by the adsorption/desorption of the gases demonstrated that this set-up is perfectly suitable for direct structural analysis at in operando conditions.

So far, experiments have carried out on one material, at cryogenic temperature and using nitrogen argon and oxygen. Further experiments are currently ongoing (proposal 25-01-965) for exploring the adsorption/desorption of the same gases on Pd-based MOFs. Considering these results and taking advantage of the cell designed and constructed at the CRG BM25 SpLine at ESFR, the idea of future work is to expand the study of the phase transitions a wide spectrum of gases (H_2, CO, CO_2, CH_4), temperatures and pressures, as well as to other nanoporous materials (zeolites, MOFs).

SCIENTIFIC IMPACT OF THE RESULTS OBTAINED IN THIS PROPOSAL

A) Articles

Salas-Colera E, Muñoz-Noval A, Heyman C, Ania CO, Parra JB, García-Granda S, Calero S, Rubio-Zuazo J, Castro GR, J. Synchr. Rad. (in press).

Ania CO, Parra JB, Salas-Colera E, Muñoz-Noval E, Garcia-Granda S, Castro GR, Unravelling the anomalous gas- adsorption of ZIF-8 using in-situ synchrotron X-ray powder diffraction, (manuscript in preparation).

B) Presentations at conferences and workshops

Parra JB, Garcia-Granda S, Castro GR, Calero S, Ania CO, Gas-induced structural deformation of ZIF-8: evidences by in-situ powder X-ray diffraction during gas adsorption, invited lecture presented in Workshop on Compliants Solids, 5-7 June 2013, Paris.

Ania CO, Parra JB, Garcia-Granda S, Calero S, Muñoz-Noval A, Salas E, Castro GR, Gas-induced structural deformation of ZIF-8: evidences by in-situ synchrotron radiation X-ray powder diffraction during gas adsorption, poster communication presented in COPS 2014 (Characterization of Porous Solids), 11-14 May 2014, Granada (Spain).

Ania CO, Parra JB, Garcia-Granda S, Calero S, Muñoz-Noval A, Salas E, Castro GR, Structural deformation of ZIF-8 upon gas uptake and release gas adsorption, to be presented at IBA-2 n Cartagena de Indias (Colombia) in May 2015.