EXPLORING GAS-INDUCED TRANSITION PHASES OF ZIF-8

PROPOSAL CODE 25-02-774

05-11 December 2012

Summary and Objetives

The objective of this proposal was to unravel the host-guest interactions of a flexible Zeolitic Imidazole Framework, ZIF-8, and to provide an evidence of the adsorption-induced transition phases occur at different gas loadings at cryogenic temperatures.

For this purpose a novel set-up was designed and performed for Synchrotron Radiation X-ray High Resolution Powder Diffraction (SR-HRPD) in transmission geometry (spinning capillary) for *in situ* solid-gas reactions and processes at isobaric and isothermal environment. The pressure and temperature of the sample were controlled from 10-3 to 1000 mbar and at 85K, respectively, although the cell allows to operate from 80 to 1000 K.

Direct evidences of structure deformation by the adsorption of Ar and N2 gases have been observed *in situ*, 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

Design and screening of novel materials with improved properties has recently gained attention in several fields, with particular emphasis settled on the new families of nanoporous crystalline materials, including Metal Organic Frameworks (MOFs), Zeolitic Imidazolium Frameworks (ZIFs), as well as zeolites and carbon adsorbents. 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 that the dimensions of the pore aperture of the solid have confirmed the flexibility in these structures [1-3]. 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 [4]. 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.

To throw some light on the origin of this anomalous behavior we have performed in-situ measurements of the X-ray diffraction patterns of this material upon controlled gas loading at cryogenic temperature. For this purpose a novel set-up was designed and performed for Synchrotron Radiation X-ray High Resolution Powder Diffraction (SR-HRPD) in transmission geometry (spinning capillary) allowing to control the pressure and temperature of the sample from 10-3 to 1000 mbar and from 80 to 1000 K, respectively.

In our experiments, diffraction patterns of ZIF-8 sample were acquired at different gas pressure and temperatures, keeping isobaric and isotherm working conditions during data acquisition. Figure 1 shows the diffractograms corresponding to nitrogen adsorption at 85 K at different gas loadings from vacuum to atmospheric pressure. 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 preselected pressure and the SR-HRPD were measured in a 2θ range from 3° to 65° corresponding to a resolution better than 0.7 Å.

As seen, outstanding differences were noticed in the patterns, with the appearance of new diffraction peaks when N_2 or Ar were dosed. The intensity of these peaks increased with the gas pressure, and correlate with the unusual gas adsorption features measured in the equilibrium adsorption 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 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 of both gases demonstrated that this set-up is perfectly suitable for direct structural analysis at in operando conditions.

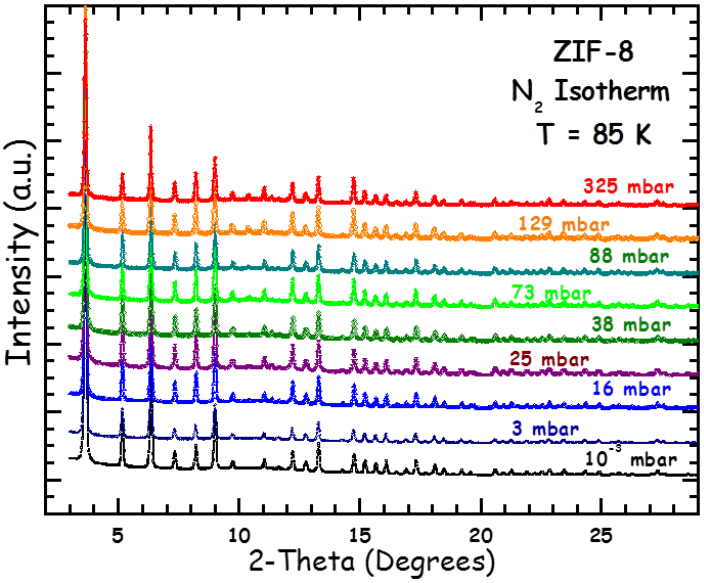

Figure 1. S-HRPD of ZIF-8 at 85K and at different nitrogen dosages (in mbar).

So far, experiments have carried out on one material, at cryogenic temperature and using nitrogen and argon. Further experiments are currently ongoing (proposal 25-02-888) for exploring the adsorption of hydrogen and carbon monoxide. 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 E, Heyman C, Ania CO, Parra JB, Garcia-Granda S, Calero S, Rubio-Zuazo J, Castro GR, Design and Development of a Controlled Pressure/Temperature Set-up for In-Situ Studies of Solid-Gas Processes and Reactions in a Synchrotron X-ray Powder Diffraction Station, J. Applied Crystallography, (submitted in June 2014).

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).