EXPLORING GAS-INDUCED TRANSITION PHASES OF ZIF-8

PROPOSAL CODE 25-01-888

18-20 June 2014

Summary and Objectives

The objective of this proposal was to continue the research initiated in previous investigations for exploring the gas adsorption/desorption induced structural transitions of a nanoporous material (ZIF-8) at different gas loadings at cryogenic temperatures.

In our previous proposals and in collaboration with the Spline at ESRF we have designed and constructed a novel experimental set-up that 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, although it is possible to operate from 80 to 1000 K (proposal 25-02-774). Direct evidences of structure deformation by the adsorption of Ar and N_2 gases have been observed *in situ*, demonstrating that this set-up is perfectly suitable for direct structural analysis *in operando* conditions.

In this proposal we aimed at extending this study to different gases (namely carbon monoxide and hydrogen), as data from equilibrium gas adsorption has pointed out to different interactions of these gases with the framework due to their size and polarizability.

Results

The design and screening of new families of nanoporous crystalline materials such as Metal Organic Frameworks (MOFs), and Zeolitic Imidazolium Frameworks (ZIFs) has recently gained attention in several fields due to their promising performance. A small group of these families of materials have revealed rather unique structural, showing interesting adsorption and diffusion of gas probes with kinetic diameters larger that the dimensions of the pore aperture of the solids [1-3]. In this context, our previous works on ZIF-8 combining high resolution gas adsorption/desorption isotherms and molecular simulations have shown that this material undergoes an outstanding structural transformation controlled by an external stimulus [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.

Aiming at understating 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 we have used the unique experimental set up available at the Spline CRG in ESRF that allows the in-situ monitoring of Synchrotron Radiation X-ray High Resolution Powder Diffraction (SR-HRPD) patterns under controlled gas dosage, pressure and temperature.

In our experiments, Synchrotron Radiation X-ray HRPD diffraction patterns of ZIF-8 were acquired at different gas pressures during the uptake (adsorption) of carbon monoxide, keeping isobaric and isotherm working conditions during data acquisition. We have also used N_2 as a probe at the same operating conditions so as to compare the obtained data with previous results obtained in our previous proposal 25-02-774.

First on all the spectrum of the sample was measured at high vacuum to obtain the pattern of the empty structure before any gas-induced transition. Then, the gas was dosed into the chamber at controlled pressures selected based on the gas adsorption

performance of the material at equilibrium conditions previously recorded in volumetric apparatus (Fig. 1). Gas dosing was carefully performed to avoid surpassing the target pressure (thus reaching the saturation limit beforehand). The SR-HRPD were measured in a 2θ range from 3° to 63° corresponding to a resolution better than 0.7 Å. The structural transition on ZIF-8 was noticed in the patterns with the appearance of a new diffraction peak at 10.5º when the gas is introduced in the porous void of the material. As previously observed for nitrogen, the intensity of this peak increased with the gas pressure, and correlate with the gas adsorption features measured in the equilibrium adsorption isotherms in a volumetric static apparatus. The pressure is however shifted downward to lower values, compared to nitrogen, which is in agreement with the stronger interaction of CO with the framework due to its marked polar moment (ca. quadrupolar moment in the case of nitrogen gas). So far, experiments have carried out on the same batch of ZIF-8. Further experiments are currently ongoing for exploring the effect of the release of gas on the structural transition (desorption) on this material. Furthermore, we plan to extend this study to other nanoporous materials (i.e., Pd-based MOFs and other ZIFs) in the future, by studying a wide spectrum of gases of strategic interest as CO_2 and CH_4 varying temperature and pressure.

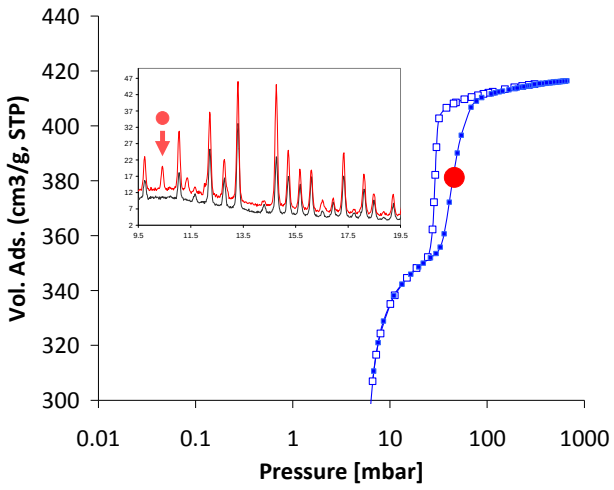

Fig.1. Changes in the synchrotron radiation-HRPD of ZIF-8 at 85K at a fixed pressure marked in the adsorption branch of the isotherm (red dot), in vacuum (black scan) and after CO dosage (red scan).

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, Design and development of a dontrolled Pressure/Temperature Set-up for In-Situ Studies of Solid-Gas Processes and Reactions in a Synchrotron X-ray Powder Diffraction Station, 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, Cartagena de Indias (Colombia) in May 2015.