Resolving the gas-induced structural changes in pure silica MFI zeolite by in-situ monitoring synchrotron XRD during gas dosing

Summary and Objectives

Our studies on equilibrium gas adsorption on different families of nanoporous materials (such as MOFs, ZIFs and zeolites) using different gases and temperatures have revealed unusual structural modifications (so called gate-opening effects) upon gas loading of these structures. The magnitude of such modifications depend on the nature (size, polarizability) of the gas probe, the temperature and the host features (composition, dimensionality, pore size) that control the host-gas interactions [1-5]. The understanding of these gas-induced structural rearrangements of nanoporous materials are crucial for their potential application in gas storage and separation purposes.

Recently, we have investigated and reported the anomalous gas adsorption features of MFI-type zeolite combining high resolution adsorption/desorption isotherms and molecular simulations. This material has a bi-stable behavior controlled by the gas pressure as external stimulus, provoking an outstanding structural transformation [1,6]. Data has suggested that the packing of the gas in the nanopore cavities of the zeolite induces a structural rearrangement of the inorganic framework; however experimental crystallographic evidences of such change are missing. Thus, the objective of this proposal was to further investigate the structural transition of this material by monitoring the structure in-operando during gas dosing under controlled conditions and using synchrotron XRD. Also, we aimed to unravel the gas-induced phase transitions as a function of the gas probe, temperature and pressures.

State of the art and background

MFI-type zeolite is of scientific and technological interest in heterogeneous catalysis, separation and purification, and lately in environmental applications [7-11]. Attempts to understand the physisorption phenomena in MFI-type zeolites has motivated a great deal of theoretical and experimental research [8-11]. This structure is characterized by two sets of interconnecting channels defined by ten-membered rings, with straight channels extending in the <010> direction and sinusoidal channels in the <l00> direction. It is well established by X-ray diffraction and NMR measurements that high-silica MFI undergoes a reversible phase transition at around 340 K, from a monoclinic to an orthorhombic structure [5,6]. The change in symmetry results only in minor changes of the framework positions and the unit cell vectors. Similar phase transitions from monoclinic to orthorhombic symmetry can also be reversibly induced by loading the zeolite with ammonia or with organic molecules [12-14].

On the other hand, gas adsorption isotherms of N_2, Ar and O_2 at cryogenic temperature in MFI-type zeolite reported in the literature have all shown a kink/step of adsorption which position depends on the nature of the gas probe used and the temperature analysis (Figure 1). The origin of this substep remains a subject of debate, and several hypothesis have been considered, including: i) a transition of the adsorbed gas from the fluid phase to a more crystalline commensurate phase [12]; ii) an intra-crystalline process rather than a solidification occurring at the pore [13]; iii) adsorbent deformations [14], and iv) a framework phase transition from the monoclinic to the orthorhombic symmetry [6]. Combining experimental measurements with molecular

simulations we have demonstrated that the structural transformation is linked to the nature of the gas adsorbed [5], although spectroscopic experimental evidences on such change in the crystalline structure are missing. To further clarify this issue and to confirm all the hypothesis, we have performed the synchrotron HRXRD patterns in operando during the gas adsorption of various gases (i.e., N_2, Ar, O_2) at cryogenic temperatures (i.e., 82-105 K), and exploring the crystalline structure at low and high temperature at which the phase transition (from monoclinic to orthorhombic) turns from reversible to irreversible.
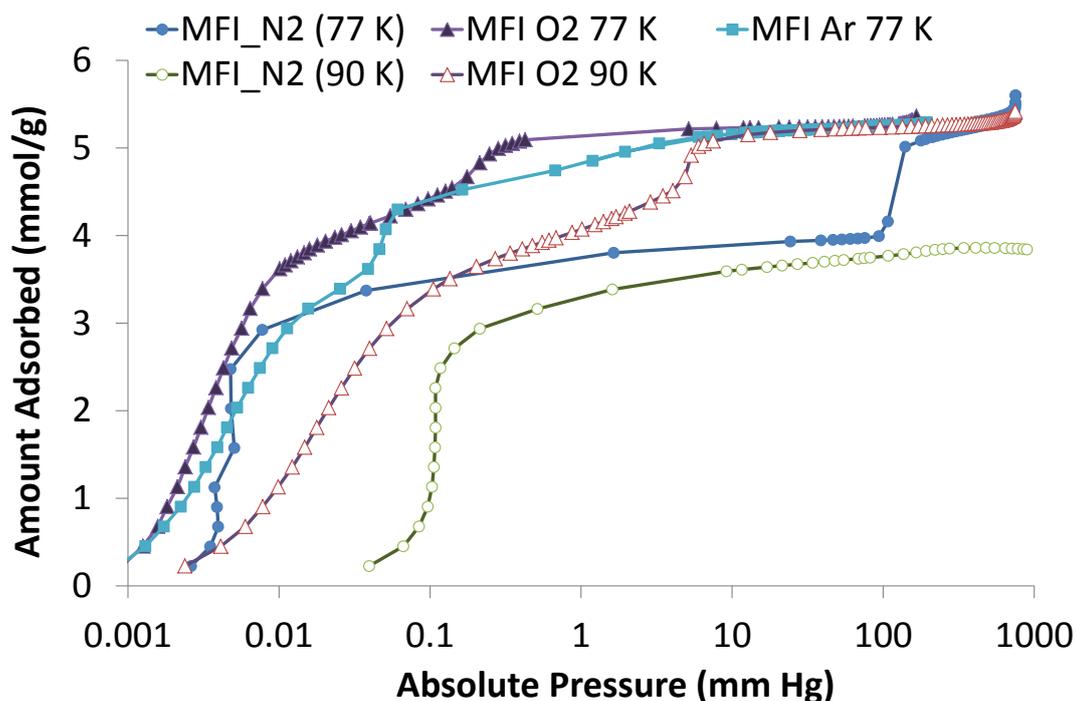
Figure 1. High resolution N_2, Ar and O_2 equilibrium adsorption/desorption isotherms of pure silica MFI zeolite (monoclinic phase) at 77 and 90 K.

Results

Figure 2 shows the corresponding spectra of the MFI zeolite under vacuum at various temperatures and loaded with the different studied gases. Initially, monoclinic MFI sample was outgassed at ambient conditions and vacuum for at least 12 hours; then the diffraction pattern of the clean structure was acquired under vacuum and at 82 K (the lowest temperature achieved with the cryocooler available at Spline Beamline BM25). Afterwards, the sample was heated up to 450 K and then cooled down to ambient temperature to verify the reversibility of the phase transition. Data showed the phase transition from monoclinic to orthorrombic, and its reversibility after heating at 450 K for 1 hour was reversible upon cooling down, in good agreement with the literature -the reversible phase transition would occur between 340 and 800 K-.

Thus, the following step was to dose the zeolite with the gases at various temperatures. We chose saturation conditions of N_2, Ar and O_2 (i.e., 800 torr) at three temperatures of: 82, 90 or 87 and 105 K, that correspond to values above and below the boiling temperatures of the studied gases at atmospheric pressure (i.e., 77 K for N_2, 87 K for Ar and 90 K for O_2). This allowed to investigate the dependence of the phase transition with the nanoconfined state of the gas in the pores of the zeolite, either above

or below the condensation temperature. It is important to remark that for each gas measurement, high resolution spectra were acquired using various detectors (acquisition conditions were very strict in a 2θ range corresponding to a resolution better than 0.01 Å using 10 detectors simultaneously). Also, the sample was evacuated at ambient conditions for at least 2 hours between each gas dosage, so as to clean the structure before a new adsorption cycle, and to confirm that the structural transition is reversible.

As seen in the HRXRD diffractograms performed on the zeolite after different gas loadings, the loading of the gas in the monoclinic structure does not seem to promote the phase transition to orthorrombic; at least not the complete transition under these experimental conditions (i.e., gas loading at cryogenic temperature and up to 1 bar), although some of the peaks of the monoclinic structure appeared shifted to peaks present in the orthorrombic one. Additionally, some new peaks were detected for some gases at certain temperatures, not indexed in either structure, that would point out to the effect of the gas packing (into a more ordered and dense state).
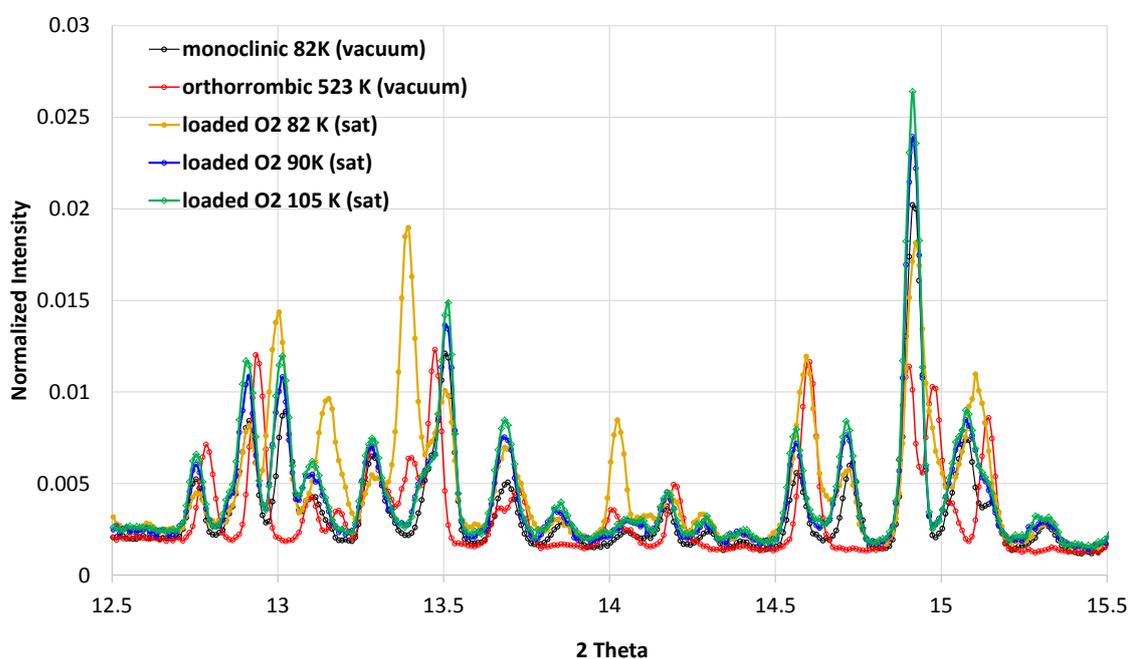
Figure 2. Example of high Resolution synchrotron X-ray diffraction patterns of pure silica MFI zeolite at various conditions: 82 K under vacuum; 523 K under vacuum; saturation of O_2 (ca. 700 torr) at various temperatures above (ca. 82 K) and below (ca. 105 K) its boiling temperature at atmospheric pressure (ca. 90 K).

Anyway, data confirmed that the adsorption substep is not attributed to the monoclinic to orthorhombic transition, and it would seem rather linked to a change in the adsorbed gas phase due to the confinement in the pores of the zeolite as suggested in the literature [13,14]. This is in good agreement with our previous work combining molecular simulations and high quality experiments that suggested a subtle interplay between the guest molecules and the flexible host structure as responsible for the substeps of adsorption [5]. Further analysis of the obtained data, including Rietveld refinement are ongoing to evaluate and ideally quantify the extent of this phase transition, and link it with the nature of the adsorbed gas (size, polarizability).

SCIENTIFIC IMPACT OF THE RESULTS OBTAINED IN THIS PROPOSAL

We have explored the gas-induced phase transitions of all silica MFI zeolite during gas uptake at equilibrium conditions and as a function of the gas properties, temperature and pressure. The use of real time monitoring of the synchrotron HRPD patterns has enabled to clarify the mechanism governing the anomalous gas adsorption features of this material. In this regard, in-situ evidences of structure deformation were obtained upon the adsorption of the gases, demonstrating that the adsorption set-up is perfectly suitable for direct structural analysis at in operando conditions [1]. The gas-induced modifications did not match with a change from monoclinic to orthorrombic phase of the solid, but rather to changes in the gas phase.

The outcome of this work is expected to be published in the forthcoming year; we also expect to present several contributions to international conferences on the fields of adsorption of nanoporous materials (i.e., meeting of the Spanish Association of Synchrotron Users to be held in Madrid 2017).

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