

High pressure CH₄ and CO₂ storage on MFI-type zeolite by in operando XRD measurements

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Summary and Objectives

Previous studies based on the 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. These 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 is 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. The studies revealed that 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 occurring inside the zeolite nanocages by monitoring the structure in-operando during gas dosing under controlled conditions and using synchrotron XRD. We studied gases of strategic impact (i.e. N₂, CO₂ and CH₄) at various temperatures at high pressure (from vacuum to 5 bar).

State of the art and background

MFI-type zeolite is of great 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 <100> 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 N₂, Ar and O₂ 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. 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.

For this, with the aim to unraveling the nature of the gas-induced stress inside the nanopore cavities on MFI zeolite upon adsorption of various gases and vapors of different composition (i.e., CH₄, CO₂) at various pressures (from vacuum to 5 bar), we have analyzed the correlation of such behavior with the nature of the gas.

In operando monitoring of high resolution powder X-ray diffraction (HRPD) patterns of the material at various temperature and high pressure conditions allow us the analysis of the response of the materials when gas is adsorbed in the structure, explaining the gas-induced structural flexibility attributed to either a transition phase of the solid or of the gas in the adsorbed state. Knowledge of the adsorption properties of MFI zeolite would help to identify further applications as catalyst and adsorbent.

Results

Figure 1 shows the corresponding spectra of the MFI zeolite under vacuum and loaded with CO₂ under different pressures at various temperatures, the temperature allowed us to reach higher pressures (due to the saturation pressure of the gas). The experiments were carried on with a unique cell specifically designed for in operando measurements under controlled conditions of gas dosage and temperature [15].

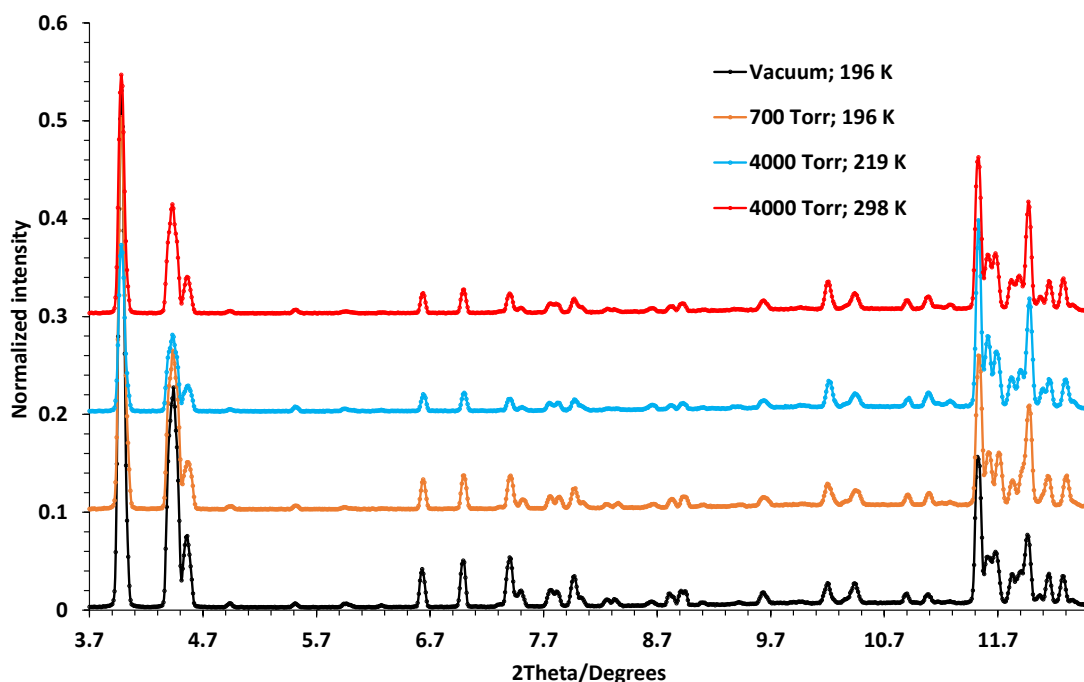


Figure 1. High Resolution synchrotron X-ray diffraction patterns of pure silica MFI zeolite at various conditions: 196 K under vacuum; 700 Torr CO₂ at 196 K, 4000 Torr CO₂ at 219 K and 298 K. The spectra are shift for clarity.

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 196 K.

The use of several pressures allowed to investigate the dependence of the phase transition with the nanoconfined state of the gas in the pores of the zeolite. It is important to remark that for each pressure 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 \AA using 10 detectors simultaneously).

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 orthorhombic; at least not the complete transition under these experimental conditions. No new peaks were detected for any pressure that would point out to non-effect of the gas packing (into a more ordered and dense state) was detected under these temperatures and pressures. Similar results were obtained dosing CH_4 and N_2 (results not shown).

Anyway, data confirmed that the adsorption substep is not attributed to the phase 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 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. 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.

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