COMPRESSION OF ZEOLITES IN „PENETRATING" FLUIDS: AN OVERVIEW

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ABSTRACT

Over the last two decades, a new light was shed on the high-pressure behavior of zeolites and on the most important mechanisms adopted by these materials to accommodate compression. However, the early discovery of the P-induced intrusion of H_2O molecules into the channels and cages of zeolites, the so-called "overhydration" effect, made clear that suitably small molecules or ions can be entrapped into the structural voids of open-framework materials in response to hydrostatic compression. This principle triggered the use of the so-called "penetrating" fluids as pressure-transmitting media for high-P experiments in diamond anvil cells. In the recent past, the results from these experiments led to the discovery of new potential applications of microporous compounds, as zeolites. The aim of this contribution is to provide a brief overview on the most important findings obtained in this field in the last few years.

Keywords: pressure, intrusion, penetrating media, host-guest interactions.

INTRODUCTION

Both natural and synthetic zeolites are exploited in several fields, ranging from the water- and soil treatment to the catalytical applications in petroleum industry, as well as the animal feeding or the nuclear waste processing. The reversible dehydration at relatively low-temperature conditions is a key feature for several technological properties and, consequently, the thermal behavior of zeolites has been thouroghly characterized. By means of different techniques, the bulk volume changes, as a function of temperature and dehydration, have been determined for the most important species, along with the structural re-arrangements concerning the framework and the extraframework cations and molecules. If compared to temperature, investigating the zeolites behavior in the high-pressure range is rather a younger subject of study. However, at least two decades of experiments have now provided a basic knowledge on the response of these open-framework materials to hydrostatic compression. The major results, summarized and discussed on the most recent reviews (e.g.[1]), allow to draw several general conclusions: 1) zeolites are not necessarily materials with high compressibility, their bulk moduli ranging from ~ 15 to 70 GPa; 2) both the framework topology and the extraframework *fillers* are main controllers of the P-induced atomic displacements and, therefore, of the bulk elastic behavior of zeolites; 3) the compression is usually accommodated by the tilting of the rigid tetrahedra around the shared oxygen hinges and, more rarely, by displacive phase transitions (e.g., in Na-mordenite[2]). The P-induced intrusion of H_2O into the zeolite crystal structures, the so-called *overhydration*[3] effect, deserves a separate discussion. This process, in fact, hinders the intrinsic behavior of the compressed zeolite: varying its crystal chemistry, the zeolite behaves as an open system. The P-induced overhydration of zeolites implies that: if 1) the H_2O molecule kinetic diameter is smaller than the free aperture (sensu Baerlocher *et al.*[4]) of channels and cages and

2) if a "structural position" is available for hosting the intruded molecule, then it is possible to use pressure as a tool for triggering the intrusion process. We can intuitevely derive that any other molecule (and possibly ions) which satisfies the previous conditions may be pressure-intruded into the structural cavities of zeolites. This consideration leads to the fascinating conclusion that we may use a combination of pressure and zeolite hosts for tailoring new systems for storing molecules in an ordered and nano-confined environment, inducing nano-confined polymerization reactions or tailoring the physical and chemical properties of the starting zeolite. The aim of this contribution is to provide a brief overview of the state-of-the-art on the behavior of zeolites when compressed in the so-called *penetrating fluids*.

EXPERIMENTAL

The experimental investigations here taken into account have been performed using in situ high-*P* X-ray diffraction as the main techinique. Both single crystals and polycrystalline samples have been studied, after being loaded in diamond anvil cells. Zeolites are often low X-ray scatterers and it is indicative that most of the studies reported below have been performed at synchrotron facilities.

A pressure-transmitting medium (usually a liquid or a gas at ambient conditions, more rarely a highly compressible and isotropic solid compound like NaCl) is needed to generate a hydrostatic pressure on the sample in the cell. For the study of the intrinsic behavior of the material, the fluid should be inert, just behaving as a pressure transfer. In contrast, the so-called penetrating fluids are those made by molecules with kinetic diameters small enough to allow the intrusion into the zeolite cavities in response to compression. Their use (pure or in a solution) as *P*-transmitting media is adopted for exploring the potential intrusion process. Elemental gases (e.g. He, Ne, Ar, Xe) or small molecules (H_2O, CO_2) are generally considered potential penetrating media, but for large-pores zeolites, even larger molecules, as e.g. ethylene glycol ($C_2H_6O_2$), may show a penetrating behavior.

Several methods are available for the pressure calibration, the most common being the measurement of the shift of the R_1 fluorescence line of standard ruby spheres excited by a visible laser light[5], loaded into the DAC along with the sample and the fluid.

RESULTS AND DISCUSSION

The first evidences of *P*-induced intrusion of H_2O molecules into the structural cavities of zeolites date back to the pioneering experiments on zeolite LTA[6], but only the investigations on the small-pore natrolite[3,7] allowed a full characterization of the intrusion process at the atomic scale. In natrolite, the indruded molecules occupy new crystallographic positions, leading to a significant structural re-arrangement of the extraframework and to a discontineous volume increase. The overhydration in the fibrous zeolites group was found to be highly dependent on the extraframework cationic composition[8]. Most commonly, the overhydration implies the filling of previously occurring partially occupied crystallographic sites, which results in smooth changes of compressibility without any discontinuity in the *V-P* data. Noble gases are often used as *P*-transmitting media for their softness (due to Van der Waals bonding) when become solid and, for this reason and for their intrinsic small kinetic diameter, are

potential penetrating media. The *P*-induced intrusion of He in LTA zeolite[9] and of Ar in natrolite (mediated by *T*)[10] has been reported to occur around 2 GPa and to be reversible in decompression. CO_2 may also be adopted as *P*-transmitting medium, *via* cryogenic loading: *T*-mediated and reversible *P*-induced adsoprtion was found e.g. in natrolite[11]. Slighlty larger molecules, which keep the liquid state (pure or in solution) at ambient conditions (as several alcohols), may also be used as penetrating media for the compression of large-pores zeolites. The *P*-induced intrusion of ethylene glycol has been reported for high-silica mordenite[12] and for SiO_2-ferrierite[13], whereas ammonia borane has been *P*-intruded in the structural cavities of silicalite-1-F[14]. The further step in this field of research is the *P*-induced (non-catalytical) polymerization of the indruded molecules. In this way mixed organic/inorganic nanocomposites materials may be obtained, showing exploitable properties of the ordered polymers nanoconfined in the structural cavities of the host zeolite, as, e.g., polyacetylene in the pores of SiO_2-silicalite[15], or zeolite ZSM-22[16], and the 2D H_2O-ethanol network in SiO_2-ferrierite[17]. Finally, the compression of hydrophobic zeolites in aqueous solutions containing (penetrating) solvated ions represents another frontier for the technological exploitation of zeolites, as the intrusion/extrusion process (and its degree of reversibility) is the source for the design of new systems for the storage and/or release of mechanical energy (e.g.[18]).

The *P*-induced intrusion process is controlled by several parameters, a part of which is independent on the crystal chemistry of the zeolite host: e.g., the kinetics of compression and the size of the sample crystals. In this respect, recent experimental findings on SiO_2-ferrierite[13] and zeolite $AlPO_4$-5[19] have clearly shown the importance of the crystal size, which can control the magnitude of the intrusion process (i.e. how many molecules are intruded at a given pressure).

CONCLUSION

The possibility to use pressure as a tool for triggering the intrusion of small molecules or ions into the structural cavities of zeolites opened a new scenario for potential technological applications of these open-framework materials. The *P*-induced intrusion processes may be adopted for tuning a vast range of properties or for the engineering of new functional materials. For a full understanding of these phenomena, the characterization of the structure-function relationship is fundamental and the goal of obtaining reliable structure models of host-guest network, based on experimental and computational data, is the challenge for the next future.

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