Pressure and Zeolite Framework Type Cooperation Effect in the Differential Absorption of Ethanol and Water from the Azeotrope Solution: the case of Si-Chabazite

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Pure silica zeolites are able, under pressure, to absorb water molecules despite their hydrophobic nature. The role of pressure has been found to be essential also in the penetration of different aqueous solutions, as mixtures of ethanol and water or of methanol, ethanol and water (m.e.w.) \cite{1, 2}. The absorption of these solutions, however, is strongly driven not only by pressure, but also by the framework type of the zeolites. Indeed, in Si-FER compressed in a water-ethanol solution, the combined effect of pressure and shape constraints induces the formation of organized arrangements of small molecules in the zeolite porosities \cite{1}. Both components penetrate zeolite cavities, but they are segregated in different channels. While the water molecules occupy only ferrierite 6MR channels, the ethanol molecules are located in the 10MR channels. The irreversibility of the process and its coupling with the supramolecular shaping effect can be a more general feature of the high-pressure (HP) behavior of other silica zeolites that can be exploited for future technological applications.

To better understand the zeolite shape-directing action in separating strongly hydrogen-bonded liquid mixtures into their constituents, the influence of different framework geometries should be considered.

In this work, a pure silica chabazite (Si-CHA) was studied by means of \textit{in situ} X-Ray Powder Diffraction (XRPD) during the penetration of an azeotrope ethanol-water solution under HP using a modified Merrill–Basset Diamond Anvil Cell (DAC). The experiment was performed at BL04-MSPD beamline of ALBA synchrotron (Barcelona, Spain). Two-dimensional patterns were recorded on a CCD camera SX165 (Rayonix), with a sample-detector distance of 160 mm, using a fixed wavelength of 0.5340 Å and 50 s collection time. Data were collected from Pamb to 2.66 GPa and upon pressure release at 0.37 GPa.

Data show that both water and ethanol penetrate Si-chabazite at both ambient and HP conditions. However, while at P_{amb} the water : ethanol ratio absorbed inside Si-chabazite is similar to that of the external azeotrope mixture, upon compression we observed a dehydration effect. In fact, at 1.84 GPa, zeolite extraframework content corresponds to a composition much richer in water than the azeotrope. The arrangement of the extraframework molecules, in comparison to Si-FER, does not present any separation between the two species. In this case, indeed, the peculiar chabazite structure, made by cages instead of separate channels, favors the interactions between ethanol and H\textsubscript{2}O molecules. At 2.44 GPa the external solution crystallizes, whereas an ideal azeotrope solution proved to crystallize at 4.8 GPa. Since pure ethanol crystallizes at about 1.9 GPa, this is a further proof of the HP-induced dehydration of the ethanol-water azeotrope. The results obtained at this pressure by XRPD were also compared to those obtained by DFT calculations.

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