# Pressure-Induced penetration of water-ethanol mixtures in all-silica Ferrierite

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The all-silica synthetic zeolite Si-FER has been compressed using ethanol/water mixture as pressure transmitting medium (PTM). Analysis of the diffraction data indicates that both components of the PTM penetrate into the zeolite cavities. First-principles molecular dynamics simulations were performed to explore the room-temperature behavior of the Si-FER/ethanol/water system. The results suggest that the organic molecules tend to form hydrogen bonded dimers, which may also be hydrogen bonded to water molecules.

**Keywords:** zeolite, Si-ferrierite, high-pressure synchrotron X-ray powder diffraction, water-ethanol separation, molecular dynamics simulations

# 1. Introduction

Ethanol produced from "biomass" is an important option in the realization of more sustainable combustion engines. However, due to its high hygroscopicity, the ethanol-gasoline mixtures (biofuels) normally adopted for vehicles are easily contaminated by water, leading to drivability problems [1]. Separating ethanol from its aqueous solution currently relies on energy intensive distillation technologies [1,2].

Zeolites can play an important role as separation membranes, but their performance strictly depends on the framework structure and composition. In particular, in biofuel production, the use of all-silica zeolites was proposed for the removal of ethanol from aqueous solutions – specifically in cases where ethanol is the minority component of such mixtures [2]. All-silica zeolites, by themselves, are very hydrophobic, but the adsorption of the organic component –

ethanol - can promote water co-adsorption through hydrogen bond formation. As a consequence, to enhance the selectivity of the zeolite in the water-ethanol separation process for this important class of applications, the desired zeolite should have a pore/channel system that well accommodates ethanol molecules but disfavors their hydrogen bonding with water.

In this context, it is also to recall that the penetration behavior of aqueous and electrolytic solutions in porous materials can be influenced by applying a moderate pressure to the system, as demonstrated, e.g. in Refs. [3,4]. Additionally, zeolites with FER topology have been recently proposed as promising media for the separation of ethanol and water [5,6]. However, to the best of our knowledge, very few structural data are available in literature on the site location of alcohol and water molecules in all-silica ferrierite (Si-FER) [7,8], especially at high pressure conditions.

To confirm and try interpreting the predicted good performance of Si-FER in separation processes involving ethanol and water, we have investigated this system at high pressure conditions by a multi-technique approach, based on the use of *in situ* synchrotron X-ray powder diffraction and first-principles modeling.

## 2. Methods and Models

#### 2.1 Synthesis of Si-FER and HP X-ray diffraction analysis

The synthesis and the characterization of Si-FER was performed as described in Ref. [7]. To determine the chemical composition of the sample, a Cameca SX 50 Electron microprobe (experimental conditions: 20 kV, beam current 2 nA) was employed on a pellet of the zeolite powder using natural minerals as standards. The thermogravimetric analysis was carried out in air on 9.62 mg of sample, by operating at a 10 °C/min heating rate from room temperature to 900 °C. The weight loss (lower than 0.5 wt.%) indicated that all the template agents used in the synthesis (i.e., pyridine and propylamine) were removed from the zeolite channels. The resulting chemical formula of the sample was [Si<sub>36</sub>O<sub>72</sub>].

The in situ high-pressure (HP) X-Ray Powder Diffraction (XRPD) experiments were carried out at the BM01a beamline at ESRF with a fixed wavelength of 0.6974 Å and a modified Merril-Bassett Diamond Anvil Cell (DAC) [9]. The pressure transmitting medium (PTM) was a mixture of ethanol:water (e.w.) (composition ratio=1:3). Pressure was calibrated using the ruby fluorescence method [10] on the non-linear hydrostatic pressure scale [11].

Structural refinement was performed at 0.84 GPa. The starting atomic coordinates of the framework for the refinement were taken from Ref. [12]. The positions of the intruded molecules were found after the inspection of the Fourier difference maps. The background curve was fitted by a Chebyshew polynomial with 20 coefficients. A pseudo-Voigt profile function [13] was applied, and the peak intensity cut-off was set to 0.1% of the peak maximum.

2.2 Molecular dynamics simulation

Water-ethanol mixtures confined inside the Si-FER framework at the GPa pressure regime were investigated by a Density Functional Theory (DFT) approach [14], with plane waves (PW) and periodic boundary conditions in 3-dimensions. The simulation cell, characterized by a framework stoichiometry of [Si<sub>108</sub>O<sub>216</sub>], was generated by taking the unit cell parameters experimentally determined for Si-FER at 0.84 GPa (a=18.588 Å; b=13.966 Å; c= 7.3596 Å) and replicating 3 unit cells along the c axis. The extraframework content of the simulation systems (4 EtOH and 7 H<sub>2</sub>O per Si-FER unit cell) was defined with the aid of the experimental data obtained at the same pressure conditions. The simulation system, characterized by the stoichiometry  $[Si_{108}O_{216}] \cdot 12$  EtOH  $\cdot 21$  H<sub>2</sub>O, was composed by 495 atoms. Only the  $\Gamma$  point of the Brillouin zone was considered. The electron-nuclei interactions were described via pseudopotentials. Ultra-soft pseudopotentials were used for O, C, H atoms [15], while norm-conserving pseudopotentials were adopted for Si [16]. Electronic states were expanded in PW up to a cutoff of 25 Ry (200 Ry for the electronic density). This theoretical scheme can well reproduce the structure of various inorganic-organic systems in a wide range of conditions [17]. The simulations were carried out at 300 K using Nose-Hoover thermostats [18]; the integration time step was 0.121 fs and a fictitious inertia parameter of 500 au was used for the electronic part of the Car Parrinello [19] equations. Data were collected and averaged over 15 ps time.

Calculations were performed with the CPMD code [20], a computational approach particularly valuable for modeling molecular/supramolecular systems confined in zeolites at both standard [21] and high pressure [22] conditions.

### 3. Results and Discussion

XRPD data provided information on the elastic behavior of Si-FER compressed in e.w (1:3). The refinement of the structure at 0.84 GPa suggested the presence of 6-8 water molecules and four ethanol per unit cell. To get a preliminary atomistic picture of the distribution of the species inside SI-FER we performed a first-principles molecular dynamics simulation by modeling 7 water molecules per unit cell. Insight on the behavior of guest molecules inside the zeolite pores may be gathered from radial distribution functions g(r), which provide valuable information on the average separation between guest species. In particular, the pair correlation functions among hydrogen and oxygen atoms may highlight the possible presence of hydrogen bonds at room temperature conditions. As a first observation, we notice that the g(r) corresponding to the distance between the oxygen atoms of two EtOH molecules (Figure 1a) presents a strong peak at about 2.8 Å, which is clear evidence of hydrogen bonds between ethanol molecules. Moreover, the peaks in the 2.5-3.0 Å region of the g(r)'s corresponding to the O<sub>EtOH</sub>-O<sub>water</sub> and O<sub>EtOH</sub>-O<sub>framework</sub> distances, although by far less intense, indicate contacts of the ethanol molecules with both framework and water oxygen atoms. The g(r)'s involving the EtOH hydroxyls protons (Figure 1b), besides the intramolecular

bonds with the EtOH oxygen (0.99 Å), are characterized by a strong intermolecular peak at 1.8 Å, which is the signature of hydrogen bonding with the nearest EtOH molecule. There is also a very low intensity peak at about 1.9 Å, suggesting weak hydrogen bonding of ethanol with framework oxygen atoms as well. No relevant interaction among ethanol hydroxyl protons and water oxygen is detected.

By focusing now on water molecules, the g(r) of water oxygen atoms (Figure 1c) indicate a strong water-water interaction with an intense peak centered at about 2.7 Å. A weaker interaction with EtOH oxygens is also present, as evidenced by the corresponding g(r), which shows a low intensity peak at 2.8 Å (Figure 1c). Also, the water oxygen-framework oxygen pair distribution, that presents a low intensity peak at 3.2 Å, indicates weak water-framework interactions. Finally, the pair distributions of the water protons, reported in Figure 1d, show the intramolecular bonding interaction at 1.0 Å and a strong peak at 1.8 Å. Altogether, these features indicate strong water-water hydrogen bonds, a relatively intense interaction with EtOH oxygen atoms at 1.9 Å and no relevant short-ranged interactions with framework oxygen atoms. On the whole, this analysis suggests the tendency of the water and of the organic system to occupy different domains of the porous host also at high pressure conditions.

It would be also important to establish whether the nature of the pressure transmitting fluid may influence the penetration of the molecular species into the FER framework, and therefore the final extraframework content of the zeolite. In previous studies, the Si-FER framework was compressed at 0.2 GPa using methanol/ethanol/water as PTM, and only water was found to be incorporated into the zeolite framework [7,8]. Specifically, 15 H<sub>2</sub>O molecules per unit cell were found into the pores, forming H<sub>2</sub>O clusters, while, remarkably, no methanol or ethanol penetration was observed, in contrast with the present case. Hence, besides framework topology, the performances of zeolites in separating liquid mixtures might strongly depend on the composition of the fluid as well.

### 4. Conclusion

The behavior of zeolite Si-FER upon compression in ethanol/water has been studied by a combined X-ray diffraction – computational approach. Results suggest that both components penetrate the zeolite cavities, but maintain a certain degree of segregation, as evidenced by the analysis of first principles molecular dynamics simulations. Work is in progress to confirm this feature, which might make Si-FER a promising framework for the separation of organic-water liquid mixtures in a broad range of conditions.

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# **Figure captions**

Figure 1. Pair distribution functions g(r) relative to: EtOH oxygen atoms, panel a; EtOH hydroxyl protons, panel b; water oxygen atoms, panel c; water protons, panel d.



Figure 1. Arletti et. al.