High-Pressure Insertion of Dense H₂ into a Model Zeolite

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ABSTRACT: Our combined high-pressure synchrotron X-ray diffraction and Monte Carlo modeling studies show super-filling of the zeolite, and computational results suggest an occupancy by a maximum of nearly two inserted H₂ molecules per framework unit, which is about twice that observed in gas hydrates. Super-filling prevents amorphization of the host material up to at least 60 GPa, which is a record pressure for zeolites and also for any group IV element being in full 4-fold coordination, except for carbon. We find that the inserted H₂ forms an exotic topologically constrained glassy-like form, otherwise unattainable in pure hydrogen. Raman spectroscopy on confined H₂ shows that the microporosity of the zeolite is retained over the entire investigated pressure range (up to 80 GPa) and that intermolecular interactions share common aspects with bulk hydrogen, while they are also affected by the zeolite framework.

INTRODUCTION

Zeolites are archetypical microporous crystalline systems both natural and synthetic with a broad range of industrial applications. Adsorption studies on zeolites at extreme conditions led some of us and other groups to develop a rich and dynamic research area. Particularly, the high-pressure insertion of simple dense molecular systems as the guest species in zeolite hosts leads to the formation of exotic guest phases and unique properties for the host framework. Once the latter is supported by inserted guests to form a "molecular spring", it resists the applied pressures. However, what would happen if the zeolites are filled by the most penetrating fundamental systems and also the most abundant element in the universe: hydrogen? Indeed, dense H₂ is a "master" and benchmark system in high-pressure sciences.

Dense, subnano confined states of H₂ could be investigated and compared to those of bulk hydrogen at extreme conditions, since these states would add to the general view of such a fundamental element. The highly penetrating character of H₂ could be also compared to other larger molecular and atomic systems to allow us to investigate the ultimate capability of filled zeolites to resist the pressure-induced pore collapse and the consequent pressure-induced amorphization (PIA). The complete deactivation of PIA can then provide information on the local structure of the framework cation, silicon in our case, at record extreme conditions. Indeed, it is of great interest to search for the extent to which the 4-fold coordination of silicon can be preserved. In bulk silica, the thermodynamic 4-fold to 6-fold transformation occurs below 10 GPa, while metastable 4-fold coordinated phases can survive at most up to 20−40 GPa. In gas hydrates, similar host−guest systems, the four-connected framework is built up by H-bonded water molecules, instead of being covalently bonded like in zeolites, and it is filled by simple gaseous molecules. Recently, CH₄-filled ice has been found to be stable up to a record pressure of 150 GPa. On the other hand, cold compression of methane clathrates at GPa has been found to lead to PIA with the amorphous form still being a host−guest gas hydrate.

We focused our work on a model, pure SiO₂ zeolite, silicalite-1 in order to avoid catalytic effects and to investigate how the pore size and shape affect the topology of the confined molecular form under pressure. Silicalite-1 is characterized by a framework of 4-, 5-, 6-, and 10-membered rings of corner-sharing SiO₄ tetrahedra forming interconnected, mutually orthogonal straight and sinusoidal channels, with ambient pressure diameters of close to 5.5 Å (see Figure 1, at 7 GPa, together with inserted H₂). Silicalite-1 is produced in crystals of several tens of microns, which makes it very suitable for optical spectroscopy studies.

In this work, we show the high-pressure insertion of H₂ in silicalite-1 up to 82 GPa. Based on synchrotron X-ray diffraction (XRD) and Monte Carlo (MC) modeling, we show that the insertion leads to an exotic glassy-like form of molecular hydrogen. H₂-filled silicalite-1 is found to be stable up to at least 60 GPa and significantly less compressible than...
the same zeolite filled by bigger molecules; this is a consequence of the more penetrating nature of H₂. The number of inserted molecules versus pressure is non-monotonic with a maximum close to two per SiO₂ unit. Raman spectroscopy shows that the framework porosity is retained up to at least 82 GPa, and it provides important clues on intermolecular interactions.

Our experimental and theoretical methods are described in the Supporting Information together with the relevant refs. 30, 31-35.

## RESULTS AND DISCUSSION

Powder XRD patterns of H₂-filled silicalite-1 were measured upon increasing pressure up to 60 GPa (Figure 2), in order to investigate to what extent the framework is stable at high pressures and also to provide inputs for MC modeling aimed to determine the amount of stored hydrogen. The large, nanometer scale, unit cell size of silicalite-1 is related to the microporosity of the framework, and it gives rise to the small 5- and 6- membered rings. In the molecular view, the red and orange sticks correspond to the chemical bonds between silicon and oxygen atoms, while the white spheres correspond to the hydrogen atoms in H₂ (the sphere radius roughly corresponds to the van der Waal’s radius of hydrogen). In the crystallographic view, the blue tetrahedra correspond to the silica tetrahedra in silicalite-1 with the red spheres showing the apical oxygens. The black dumbbells represent the inserted H₂ molecules. A 2 × 2 × 2 unit cell is considered here for the sake of clarity.

Figure 1. Structure of H₂-filled orthorhombic silicalite-1. Left: principles of MC modeling in the grand canonical ensemble. Like in real experiments, a zeolite material is set in contact with an infinite reservoir of bulk H₂. The purple shaded area denotes the unit cell volume, while the blue dashed line indicates the periodic boundary conditions. Right: molecular (top) and crystallographic (bottom) view of H₂ inserted in silicalite-1 at room temperature and P = 7 GPa. In addition to the channels, some hydrogen molecules occupy the cages enclosed by the small 5- and 6- membered rings. In the molecular view, the red and orange sticks correspond to the chemical bonds between silicon and oxygen atoms, while the white spheres correspond to the hydrogen atoms in H₂ (the sphere radius roughly corresponds to the van der Waal’s radius of hydrogen). In the crystallographic view, the blue tetrahedra correspond to the silica tetrahedra in silicalite-1 with the red spheres showing the apical oxygens. The black dumbbells represent the inserted H₂ molecules. A 2 × 2 × 2 unit cell is considered here for the sake of clarity.

Figure 2. Left panel: selected powder XRD (λ = 0.4828 Å) patterns of H₂-filled silicalite-1, measured upon increasing pressure. A broad Compton scattering background due to air and diamonds has been subtracted. Right panel: experimental pressure behavior for the relative to ambient pressure unit cell volume of H₂-filled silicalite-1 (filled circles). Error bars are within the size of the circles. Red line: compression curve for Ar and CO₂-filled silicalite-1. Black line: equation of state for silicalite-1, measured in a nonpenetrating pressure transmitting medium silicone oil, where amorphization has been found to occur below 10 GPa.

by oxygen was retained at record pressures among all known group IV compounds, except carbon. Indeed, the thermodynamic transformation pressure from 4-fold to 6-fold coordination in bulk silica is lower by 1 order of magnitude. LeBail fitting of the XRD patterns (Figure S4) was used to obtain the pressure behavior of the unit cell volume of H₂-filled silicalite-1 (Figure 2) normalized to its ambient pressure value. We can compare this compression curve with those observed for other penetrating simple gaseous systems such as Ar and CO₂. The most striking result is the much higher relative volumes of up to 24% at 25 GPa measured for H₂-filled silicalite-1 than for Ar or CO₂ filled silicalite-1, clearly indicating that H₂ is much more penetrating than the other two larger systems. Also, the compression curve of H₂-filled silicalite-1 shows an anomaly. Indeed, a quasi-horizontal inflection point appears at around 19 GPa. Above this point, the curve is convex rather than concave, up to about 50 GPa. This anomaly is suggestive of substantial pressure changes in the filling of silicalite-1 by H₂, a hypothesis that can only be tested on the grand canonical ensemble-based MC model, whose main outputs are the spatial distribution and the number of inserted molecules per unit cell.

In Figure 1, we report the structure of H₂-filled orthorhombic silicalite-1 at 7.0 GPa, obtained by combining the experimentally determined lattice parameters with MC modeling. The zeolite framework is entirely filled by guest H₂ molecules, 127 per unit cell. The state of inserted hydrogen is remarkable. Indeed, this is a disordered, dense form within the whole investigated pressure range by XRD and MC, that is up to 60 GPa. Also, considering the very large density reached in nanoconfined H₂ at such extreme pressures, we assume this disordered form to be glassy-like rather than liquid-like. This type of disorder is supported by the intermolecular radial distribution function (RDF), reported in Figure S2 for a...
selected pressure of 7.0 GPa. As expected for glassy-like, that is disordered configurations, the RDF displays a strong peak at short distance (here about 2.6 Å) corresponding to the nearest neighbors’, followed by additional much weaker and broader peaks at increasing distances. Overall, the different peaks are broad with an amplitude that strongly decreases with increasing the intermolecular distance. The calculated number of inserted H₂ molecules per unit cell of silicalite-1 by MC as a function of pressure clearly exhibits a maximum (Figure 3, left panel), which corresponds to the anomaly experimentally observed for the pressure behavior of the unit cell volume. The maximum is equal to about 174, and it is located at around 34 GPa. The very low compressibility of H₂-filled silicalite-1 in the 15–25 GPa pressure interval is now found to be due to H₂ rapidly entering silicalite-1 to a greater and greater extent upon increasing pressure in this range; here, the filling of H₂ hinders the reduction of the host framework volume by strongly reducing the compressibility of the pores. Then, above 30–40 GPa, some amount of previously inserted H₂ is extruded and the volume of silicalite-1 decreases as a result of the combined effect of guest extrusion and normal compression of the filled framework material. H₂-filled silicalite-1 is thus a hydrogen-rich material, with H₂ being physisorbed by the zeolite and an overall pressure-dependent chemical composition \( \text{SiO}_2(H_2)_x \), with \( x = 1.32–1.82 \). In fact, this gas content is substantially greater, in terms of the number of stored guest molecules, than that experimentally observed so far in any gas hydrate phase.
under any pressure-temperature condition, as may be expected as zeolites contain both cages and channels.

At least two remarkable differences emerge between H2-filled silicalite-1 and the filling of this zeolite with larger simple systems such as Ar and CO2. First, the maximum number of confined H2 molecules exceeds that for bigger molecules by a factor of 3−4. Second, H2 is so much more penetrating that even the cages with small openings of 1.4−3.0 Å diameter built up by 5- and 6-membered rings are well filled in this case. We found that the number of H2 molecules in these cages is equal to 20 per unit cell over the whole investigated pressure range, which is 11−16% of the total amount of inserted molecules. Also, we found that multiple filling of some cages occurs, similarly to several gas hydrates. Interestingly, the non-monotonicity for the pressure behavior of the filling appears to be entirely due to molecules inserted in the channels. All this explains why the volume of the zeolite is so much larger when H2, rather than bigger guests, is inserted into the framework.

Importantly, the nearest neighbor’s intermolecular distance for confined hydrogen is larger than that for bulk hydrogen (Figure 3, right panel) by a few percent, indicating that the H2-silicalite-1 interaction adds a negative term to the local pressure.

The Raman spectroscopy investigation provides direct information on dynamical properties of the confined dense form of hydrogen. In Figure 4, we report waterfalls of selected Raman spectra of the H2 vibron for H2/silicalite-1 samples, measured upon increasing pressure on silicalite-1 crystals up to 82.5 GPa. In the spectra, we observe the pure H2 peak due to bulk hydrogen layers surrounding the crystals and several blue-shifted extra peaks which can be easily attributed to confined dense H2. The blueshift, which increases with pressure, is the net result of the modified intermolecular interactions in confined hydrogen and the interaction between the guest molecules and the internal walls of the porous host. Spectra measured on larger silicalite-1 crystals show up to 4−5 partially resolved peaks for confined hydrogen (Figure 4, left panel), likely to be ascribed to H2 guest molecules located on distinct host crystallographic sites of silicalite-1 and, as a consequence, experiencing different interactions. These peaks are much broader than the peak of bulk H2 and they broaden upon increasing pressure till they merge. This finding is compatible with confined hydrogen being highly disordered around the different crystallographic sites corresponding to the distinct peaks, in full agreement with the combined XRD/MC outcome where confined H2 is indeed found to be in a glassy-like state.

In Figure 5, we report the pressure shift of the H2 frequency for the most intense peak in confined H2 and for bulk H2 measured in this work up to 82.5 GPa and also for isolated H2 impurities in three crystalline matrices: Ne, Ar, and D2. The pressure behavior for the confined H2 frequency is remarkable; it is systematically higher than that of the Raman frequency for pure H2 and, more importantly, in both cases we observe a maximum, which is located at around 50 GPa in confined H2 and 35 GPa in pure H2. In addition, in confined hydrogen, a frequency jump occurs around 62 GPa, beyond the pressure range of our XRD investigation, which probably relates to a major structural change in silicalite-1, such as a yet unknown phase transition. The origin of the maximum in the H2 frequency for confined hydrogen can be easily traced back to the H2−H2 vibrational coupling (and references therein.)

Figure 5. H2 frequency vs pressure for different materials and compounds. For this work, values for confined in silicalite-1 (full dots) and bulk H2 (open dots) (see text for details). Black lines: guides for the eye through these two data sets. Error bars are mainly due to the fitting procedure of peaks for confined H2. Other lines: pressure shift for H2 as a single molecule impurity in Ne (black), D2 (blue), and Ar (green) matrices, respectively. Orange line: pressure shift for the IR active H2 frequency in pure hydrogen. See also S1). The Raman frequency being blue-shifted in confined H2 and the maximum being at higher pressures with respect to bulk H2 suggest that vibrational coupling is weaker in the confined form. This is due to the larger intermolecular distance (see Figure 3) and to the reduced number of H2 neighbors. An extreme case in this respect is that of molecules in the cages of silicalite-1, where the number of H2 neighbors drops to 1 or 0 and the vibrational coupling is nearly or entirely switched off. This case likely corresponds to the highest frequency components in the Raman frequency distribution for confined hydrogen (Figure 4). The Raman spectra of the rotational peaks (Figure S5) show that confined H2 is a near free rotor, the rotations of which are somewhat more hindered than for pure hydrogen.

CONCLUSIONS

Our investigation uncovered an exotic form of dense hydrogen inserted in a zeolite at pressures up to 80 GPa. What is the Mbar/multi-Mbar fate of H2-filled zeolites? What is the fate of silicon coordination in gas-filled framework materials and, more generally, of host−guest systems where the host is a covalent or H-bonded network and the guest is a simple atom or molecule, and what is the potential to synthesize novel H-rich systems in this way? All these questions among others build up an entirely unexplored field, initiated here and left to future intriguing studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c02177.

Experimental and computational methods; supplementary GCMC results; supplementary XRD results; H2−H2 vibrational coupling; and supplementary Raman spectroscopy results (PDF)
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