

LESSONS FROM ZEOLITES: WHAT WE CAN LEARN FOR DESIGNING IMPROVED HYDROGEN STORAGE MATERIALS

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ABSTRACT

Some of the factors that determine the adsorption sites for hydrogen and strength of its interaction with the host material were determined from systematic studies of the hindered rotor transitions of the adsorbed hydrogen molecule by inelastic neutron scattering in a great number of different zeolites with a variety of ion exchanges. Binding of H₂ is found to be governed by a complex combination of the type, charge and size of the cations, their coordination to the host framework, and their accessibility to the hydrogen molecule as well as the relative acidity of the framework, and these findings can provide important criteria for the development of more effective hybrid materials for hydrogen storage. We find, for example, that binding of hydrogen in these charged frameworks is in general strongly enhanced relative to those that are neutral (as are most MOF's), and is strongest at highly undercoordinated, and exposed extra framework cations such as Li⁺ in LiA and in LiX. Molecular chemisorption of H₂ at metal sites introduced post-synthesis into porous materials as observed in Cu-ZSM-5, however, would appear to offer the greatest increase in hydrogen heats of adsorption short of dissociative binding.

Keywords: Zeolites, Hydrogen Storage, Neutron Scattering

INTRODUCTION

The interaction of the hydrogen molecule with a porous host material is both of fundamental and enormous practical importance, particularly in view of the need to develop more suitable materials for the storage of hydrogen as a fuel for mobile applications than those currently available. The class of nanostructured materials has greatly expanded in recent years [1] and now includes porous materials with a wide variety of pore sizes and shapes, which can, in many cases be tailored to a particular application in catalysis, separation or gas storage. Materials with a large degree of crystallinity such as coordination polymers [2] and zeolites [3] are especially desirable on account of their relative stability and their uniformity of molecular binding sites, or catalytically active sites. Porous materials for potential use in hydrogen storage applications should have a pore structure with dimensions that do not exceed that of two or three times the kinetic diameter (2.9 Å) of the H₂ molecule, as do zeolites and some metal-organic framework compounds [4]. Zeolites, however, do not have the required surface area (> 3000 m²/g) for hydrogen storage based on physisorption [5], because of the very high density of their framework, but are nearly ideal as a platform for molecular level studies of the interaction of hydrogen with porous host materials. The reason for this is their well-defined structure and amenability to systematic changes by means of ion exchange, or of the Si-Al ratio. This should enable us to determine some of the factors that could lead to an increase in binding energy for hydrogen in other porous materials, which is urgently required if physisorption is to be utilized for hydrogen storage at room temperature and low pressure in currently available porous materials.

EXPERIMENTAL

Inelastic neutron scattering spectra were obtained at low temperatures (1.5 to 15 K) after in-situ adsorption at 77 K of a predetermined amount of H₂ (e.g. one molecule per supercage)

from an external gas handling system on appropriate spectrometers at different neutron sources as previously reported [6,7].

RESULTS AND DISCUSSION

The transitions between the rotational energy levels of the adsorbed H₂ molecules are extraordinarily sensitive to the environment at the binding site, and their frequencies can be taken as an approximate indication of the strength of the guest-host interaction at this specific site. In fact, the transition between the two lowest energy levels (ortho-para H₂ for the free rotor) is a rotational tunneling transition, whose energy has an approximately exponential dependence on the height of the barrier to rotation. Rotational tunneling transitions covering more than two orders of magnitude in frequency have been observed for bound hydrogen, from 120 cm⁻¹ for the free rotor to less than 1 cm⁻¹ for coordinated molecular hydrogen in some cases.

Free rotation of the hydrogen molecules is barely perturbed on most carbon surfaces[8], for example, while even zeolites with high Si/Al ratio, and hence few Brønstedt acid sites shift the frequency of the lowest rotational transition down from 120 cm⁻¹ to around 90 cm⁻¹ [6]. Direct interaction with extraframework cations can have a much more significant effect as shown for H₂ in LiA (Fig.1). A peak at very low frequency (1 meV, or 8 cm⁻¹) indicates the existence of an unusually strong binding site, while the fact that its intensity does not increase with H₂ loading above 1H₂/supercage means that just one of these types of site exists in the structure. It can therefore readily be associated with undercoordinated type II or III cations in or near the eight-ring window.

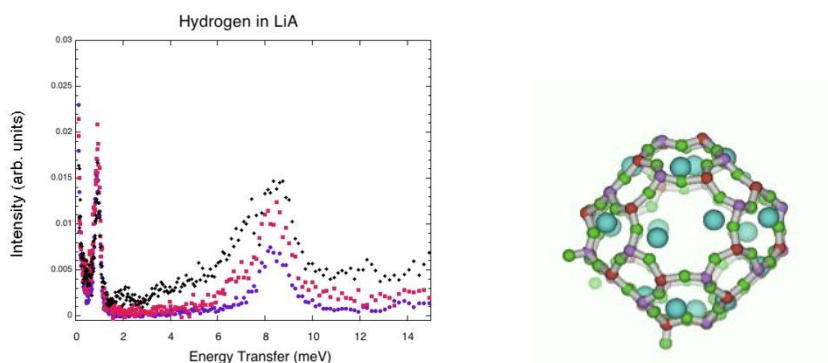


Figure 1. (a) INS spectra of H₂ in fully exchanged Li-A as a function of loading (1, 2 and 4 H₂ per supercage), (b) Li⁺ cation location in zeolite A from MD simulations [6], the 8-ring window.

Binding at type I cations in the six-ring window gives rise to the broad band near 8 meV which is indicative of a much weaker interaction. These cations are coordinated to at least three framework oxygen atoms, whose size may also prevent a more direct approach of the hydrogen molecule. Divalent cations (e.g. Cu²⁺, Ni²⁺, Ca²⁺) are somewhat more effective (rotational tunneling transitions as low as about 18 cm⁻¹) in the same type six-ring site than the monovalent cations, but not as much as, for example, Li⁺ and Na⁺ in undercoordinated type II or III sites. In all these cases, however, the extra-framework cations in zeolites exhibit stronger affinity to H₂ than the same type in-framework metal site in MOF's even those with formally open binding sites such as the Cu site in HKUST-1.

The pronounced effect of having a very open coordination environment of the metal site is apparent in the case of Cu-ZSM-5, where H₂ forms a molecular hydrogen complex by way of a direct electronic interaction with Cu(I) in the same manner as organometallic metal dihydrogen complexes. The INS spectrum for H₂ in Cu-ZSM-5 exhibits a set of rotational tunneling peaks at a very low frequency of about 1 cm⁻¹ (Fig. 2a), which can be accounted for

by our model calculation [9] of Cu(I) sites in Chabazite (Fig. 2b). Our results show that the hydrogen molecule is bound to a Cu which is coordinated to just two framework oxygen atoms. This Cu(I)-H₂ complex also has the structural characteristics found in organometallic system, i.e. an activated, elongated H-H bond (0.80 Å), and the very short H-metal distances (1.65 Å) necessary for a direct electronic interaction. H₂ merely physisorbs at the six-ring site (Fig. 2c) where in the case of CuNaA we find the rotational tunneling transition at about 18.5 cm⁻¹.

These findings are in stark contrast to what has been observed for so-called open metal sites in MOF's, where the slightly enhanced binding energies for hydrogen arise simply from enhanced polarization interaction with the metal because of the fact that the H₂ molecules are much too far away (typically ~2.5Å) [10] from the metal center to facilitate orbital overlap. In-framework metal sites in zeolites, such as Ti in Ti-SBA-15, are similarly ineffective but can apparently be activated at elevated hydrogen pressures [11].

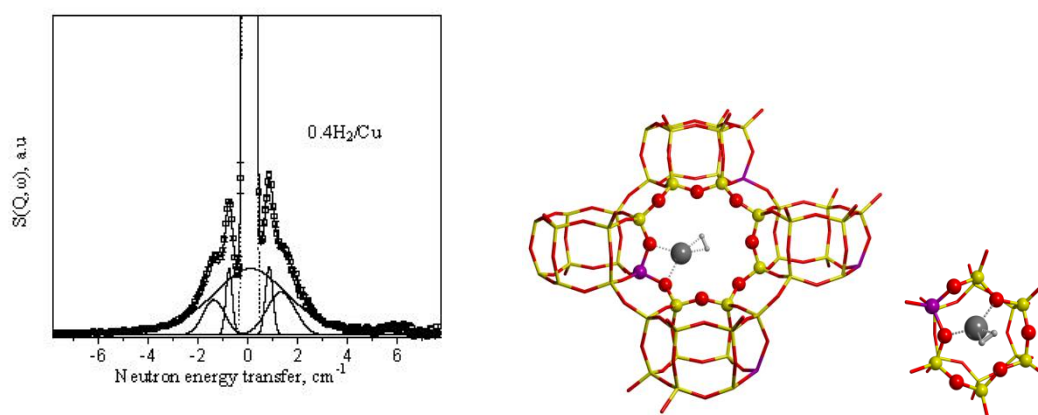


Figure 2. (a) Low frequency INS spectrum of H₂ in Cu-ZSM-5 [6]; model structures for H₂ (b) coordinated to Cu(I) in chabazite, or bound (c) in the six-ring window[9].

The obvious realization that charged frameworks, or the presence of charged species appreciably enhances H₂ binding in MOF's has in fact been demonstrated for some anionic MOF's [11] which were found to have values of the isosteric heat of adsorption some 50% greater than that of typical neutral MOF's. It is, however, difficult to see how metal sites in MOF's can be made more accessible to hydrogen molecules, so that post-synthesis modification would appear to be the main route to greater utilization of the much stronger affinity of metals for hydrogen, a strategy which is currently being pursued by a number of groups.

CONCLUSION

The most important conclusions from this work relate to the understanding of the role of metal binding sites in coordination polymers for hydrogen storage. Comparison of the present results with those obtained on metal-organic framework compounds containing the same metals (Zn, Cu, Ni) as some extra framework cations in zeolites leads to several important observations that are highly relevant to the design of porous materials for hydrogen storage. These findings include that extra-framework metal ions are more effective than in-framework metal atoms, that the metal ion should be highly undercoordinated for strong binding of H₂ up to coordination of dihydrogen, and should not be partially blocked by surrounding atoms. We have also demonstrated that the presence of charged species, and charged frameworks offers an appreciably advantage over neutral MOFs, and as do the smaller pore sizes in zeolites relative to some MOFs with very large pores.

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