

Lattice Gas Model for H₂ Adsorption in Nanoporous Zinc Hexacyanometallates

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Zinc hexacyanometallates Zn₃A₂[M(CN)₆]₂ with different exchangeable alkaline cations A⁺ and framework transition metals M constitute an excellent model system to study H₂ adsorption in nanoporous solids. A lattice gas approach, based on experimental data and simple considerations on the position and energies of adsorption sites, is proposed. Coverage and adsorption enthalpies are calculated and compared with experimental results. The interplay of three necessary conditions for H₂ storage in porous solids—free volume to accommodate guest molecules, charge centers to bind them, and fast diffusion during adsorption or desorption—is discussed.

1. Introduction

High-density storage is probably the main challenge for the wide use of molecular hydrogen as a secondary energy bearer, especially for mobile applications.^{1,2} The limitations of gas and liquid phases are well known. Adsorption in solids with extended internal surfaces and the formation of chemical hydrides appear as the most promising alternatives.^{3–8} At present, none reported material meets the minimal technological requirements: fast and reversible adsorption and desorption of 6 wt % at moderate temperatures and pressures.

Porous zinc hexacyanometallates Zn₃A₂[M(CN)₆]₂ have been studied as potential H₂ storage materials.^{9–11} Actually, their reported adsorption capacity is quite far from the established goal. However, systematic variation of framework transition metals M and exchangeable alkaline cations A⁺ provides an excellent model system to understand H₂ storage in porous solids.

The structure of these compounds is well known.^{12–14} They crystallize with a hexagonal unit cell containing 6 formula units, with cell parameters $a_H \approx 12.5$ Å, $c_H \approx 32.6$ Å, only slightly dependent on the involved metals M and A. Their network of pores is formed by six ellipsoidal cavities per unit cell, with dimensions close to $15.5 \times 11.1 \times 7.9$ Å. Six elliptical windows of about 6.8×8 Å communicate neighbor cavities. Windows are formed by two octahedra [M(CN)₆] with tetrahedral coordination to Zn atoms. Approximating^{12,13} C≡N groups by cylinders of radius 1.4 Å, windows resemble small tubes of internal dimensions $4 \times 5.2 \times 2.8$ Å. In Figure 1, elaborated with data taken from a previous work,¹⁴ two ellipsoidal cavities are shown (left). The same cavities, now rotated (right), show their common elliptic window.

For M = Co, the cation-free isostructural hydrophobic composition Zn₃[Co(CN)₆]₂ is obtained. In this case windows have zero net charge. The dipolar electric field, resulting from the excess of electron density in the C≡N bonds and the deficit on the metal sites, is too weak to bind water dipoles, but it is inhomogeneous enough to create an electric field gradient

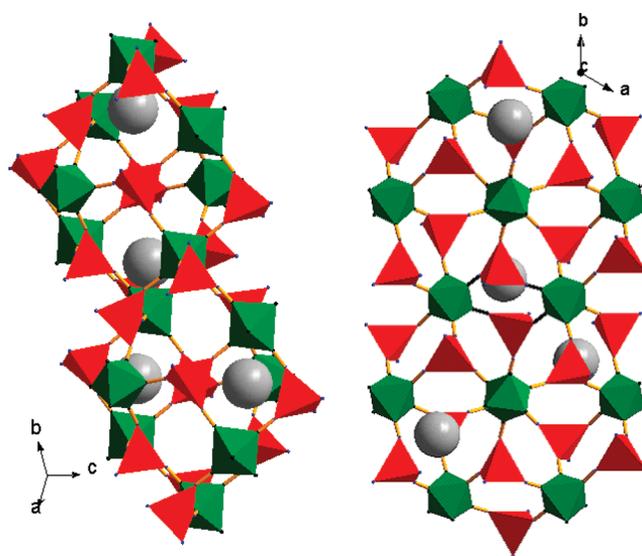


Figure 1. Porous framework for the materials under study, formed by octahedra [M(CN)₆] with tetrahedral coordination to Zn atoms. The exchangeable cations are represented by spheres. Left: two ellipsoidal cavities can be appreciated. Right: The same cavities, now rotated, are shown to be communicated by an elliptic window.

attracting quadrupolar molecules, like H₂ and CO₂, as shown in adsorption experiments.^{10,11}

In hexacyanometallates with M = Fe, Ru, Os windows have an average negative charge $-2e/3$. Two exchangeable cations A⁺ per cavity occupy two of six equivalent sites close to windows, most probably at opposite windows,^{12,13} as shown in Figure 1. Water molecules are primarily bound to charge centers and then to other water molecules through hydrogen bonding interactions. In hydrated samples, the distance between cations calculated from reported atomic positions^{12–14} are 3.21 Å for Na, 5.57 Å for K, and 5.49 Å for Rb.

A systematic study of H₂ adsorption in the hexacyanometallates Zn₃A₂[M(CN)₆]₂, with A = Na, K, Rb, and Cs and M = Fe, Os, Ru, together with the cation-free isostructural composition Zn₃[Co(CN)₆]₂, taken for comparison, has been presented in refs 10 and 11.

As shown by thermogravimetric analysis,^{10,11} continuous reversible dehydration occurs below 200 °C. Dehydration

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