

Hydrogen Storage in Porous Cyanometalates: Role of the Exchangeable Alkali Metal

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The hydrogen storage in zeolite-like hexacyanometalates with different exchangeable alkali metals within the cavities was studied. The H₂ adsorption isotherms were recorded at 75 and 85 K in order to estimate the involved adsorption heats using the isosteric method. The electric field gradient within the porous framework favors the hydrogen adsorption in the materials under study but also could lead to kinetic effects for the pore filling. Such effects were particularly pronounced for sodium among the studied compositions: Zn₃A₂[Fe(CN)₆]₂ (A = Na⁺, K⁺, Rb⁺, Cs⁺) and Zn₃[Co(CN)₆]₂. For Na⁺, a strong interaction with the H₂ molecule takes place, where appreciable kinetic effects even at 258 K are observed. For Zn₃[Co(CN)₆]₂ (rhombohedral phase) where the cavities are free of exchangeable metal and, in consequence, have a weak electric field gradient on their surface, the largest hydrogen storage capacity, close to 12 H₂ molecules per cavity (1.82% by weight), was observed. The hydrogen adsorption in these materials involves adsorption heats in the 6–8.5 kJ/mol range, following the order K > Rb > Cs ≈ Zn₃[Co(CN)₆]₂. The porous framework of this family of materials is formed by ellipsoidal cavities communicated by elliptical windows. The alkali metals are sited close to the windows. The pore accessibility and pore volume were evaluated from CO₂ adsorption isotherms recorded at 273 K. The free volume was found to be accessible to the CO₂ molecule for all of the studied compositions. According to the obtained isotherms the stabilization of the CO₂ molecule within the pores is caused by the electrostatic interaction between the electric field gradient at the cavity and the adsorbate quadrupole moment. The estimated strength for the guest–host interaction and the accessible pore volume follow the order Na > K > Rb > Cs. The largest accessible pore volume was found for Zn₃[Co(CN)₆]₂, close to 8 CO₂ molecules per cavity (28% by weight), but with the weaker guest–host interaction. The materials under study were characterized from X-ray diffraction, thermo-gravimetric, infrared, and Mössbauer data. The obtained results shed light on the role of the electric field gradient at the cavity for the hydrogen adsorption.

1. Introduction

The role of greenhouse gas emissions from fossil fuel combustion on the climate changes related to global warming is nowadays well accepted. This fact, together with the increasing energy demand and the progressive decrease for the worldwide reserve of these traditional energy sources, are forcing us to find environmentally compatible alternative energy resources.¹ Related to the clean combustion of hydrogen and its high heating value (572 kJ/mol), the development of an energetic technology based on hydrogen appears to be one of the most promising options, particularly for vehicular applications.² In that sense, the main fundamental and technological challenge is to find an appropriate method for molecular hydrogen storage, with high gravimetric capacity, of at least 6 wt %, and fast adsorption–desorption kinetics at temperatures below 373 K.³ The highest hydrogen storage capacity has been reported through the use of chemical and metal hydrides but, with these materials, the hydrogen desorption usually requires high temperatures (>500 K) and reversibility is not always

guaranteed.³ These features are the main handicap of these storage media. An attractive option is the physical adsorption due to its reversibility, but with the inconvenience, to date, of relatively low gravimetric density of adsorbed hydrogen.⁴ Several families of porous materials have been evaluated for hydrogen storage, among them, carbon-based materials,⁵ zeolites,⁶ and metal-organic frameworks.^{7–9} For zeolites, the presence of exposed highly polarizing cations in channels and cavities has been related to the possibility of attaining appropriate stabilization for the hydrogen molecules within the microporous structure.^{4,6,10} More recently, porous coordination polymers, of Prussian-blue type, have received certain attention as prototypes of materials for hydrogen storage.^{11–16} The relatively high ability that these materials show for hydrogen storage has been attributed to the availability of free coordination sites for the nitrogen-bound metal sited at the pore's surface, in their anhydrous phases.^{11–16} However, the role of the pore surface electric field gradient for the hydrogen storage remains to be clarified. A high electric field gradient could favor a higher excess for the hydrogen molecule within the cavity but also could be contributing to reduce the hydrogen diffusion rate through the porous framework delaying the cavities filling. The role of the alkali metal sited within the pore for the hydrogen adsorption has been explored in alkali metal exchanged zeolites,^{4,6,17} but not for porous coordination polymers. In this contribution, we are reporting the hydrogen adsorption in a family of porous hexacyanometalates, Zn₃A₂[Fe(CN)₆]₂, where

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