Hydrogen Storage in Zeolite-Like Hexacyanometallates: Role of the Building Block

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Received: March 31, 2008

Hydrogen storage in zeolite-like hexacyanometallates, $Zn_3A_2[M(CN)_6]_2$ with A = K, Rb, Cs, and M = Fe, Ru, Os, was studied. In a previous article, we have reported the role of the exchangeable metal (A) for M = Fe on the H₂ adsorption. This contribution concerns to the effect of the molecular block, $[M(CN)_6]$, on the recorded H₂ adsorption isotherms and the corresponding adsorption heats. This family of porous materials can be considered as octahedral anionic blocks, $[M(CN)_6]^{4-}$, assembled by zinc (2+) atoms linked at their nitrogen ends. The porous framework topology was described from the refined crystal structures. In the resulting 3D network the zinc atom is found with a tetrahedral coordination. This leads to formation of ellipsoidal cavities, of about 12.5 × 9 × 8 Å, which remain communicated by elliptical windows. The H₂ adsorption heats follow the order: Os > Ru > Fe. The building block contribution to the H₂ adsorption potential takes place through the charge delocalization from the inner metal (M) to increase the electric field gradient at the cavity surface. The CO₂ adsorption isotherms are also conclusive on the contribution of the building block to the cavity adsorption potential. All of the studied samples were characterized from X-ray diffraction, infrared, and thermogravimetric data.

1. Introduction

The progress of human civilization is closely related to the availability of energy sources. From the first industrial activity for exploitation of petroleum, in 1859,¹ and then its processing to obtain different derivatives, practically all of the known technological advances have been linked to the use of this fossil fuel. Petroleum and other fossil fuels are nonrenewable energy resources, and for the next decades a definitive decline in their availability and production are expected. In addition, the combustion of fossil fuels leads to CO₂ emission, which is responsible for the global warming and of the related climate changes.² From these facts, the research and development activities on renewably energy sources have received increasing attention in the last decades. In this sense, sunlight harvesting appears to be most attractive solution.³ However, for applications like automotive vehicles, and also as an energy storage medium, a secondary energy bearer is required. Hydrogen is a promising secondary-energy bearer related to its clean combustion (produces water as byproduct) and high heating value (572 kJ/mol). For such applications, the main fundamental and technological challenge is to find appropriate methods for hydrogen storage. Hydrogen, in its molecular form, H₂, can only be maintained in liquid state below 32.7 K (the H₂ critical temperature), independent of the applied pressure, and the liquefaction process consumes about 40% of the energy to be generated. H₂ storage at high pressure appears to be impractical, for a pressure of 345 atm. a density of 15/g is obtained, relatively low compared with 70 g/L for liquid state. Regarding the hydrogen storage

for vehicular applications, the U.S. Department of Energy (DOE) has set a series of targets, nowadays worldwide accepted as reference targets, which include a gravimetric storage capacity of at least 9 wt % (2015 target), and with an appropriate adsorption–desorption kinetics at temperatures below 373 K to allow a quick and safe refueled process.⁴

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 of high temperatures (>500 K) and the reversibility is not always guaranteed.⁵ 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.⁶ Several families of porous materials have been evaluated for hydrogen storage, among them, carbon-based materials,7 zeolites,8 and metal-organic frameworks.9-11 For zeolites, the presence of exposed highly polarizing cations in channels and cavities has been related to the possibility of attaining an appropriate stabilization for the hydrogen molecule within the microporous structure.^{6,8,12} More recently, cyanide-based porous coordination polymers have received certain attention as a prototype of materials for hydrogen storage.^{13–24} The relatively high ability that these last materials show for the hydrogen storage has been attributed to the availability of free coordination sites for the nitrogen-bound metal site at the pores' surface, in their anhydrous phases, and/or to an appropriate electric field gradient within the cavity.^{13–23} From a recent study, we have reported on the role of the exchangeable alkali metal for the H₂ storage in zeolite-like hexacyanoferrates (II), Zn₃A₂[Fe(CN)₆]₂ (A = K, Rb, Cs)²¹ However, to the best of our knowledge, the effect of the building block on the H₂ adsorption potential in this family of materials has not been reported. The H₂ adsorption isotherms at 75 and 85 K were now recorded for $Zn_3A_2[M(CN)_6]_2$ with M = Fe, Ru, Os. The estimated values

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