

Hydrogen Storage in Porous Transition Metals Nitroprussides

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Transition metals nitroprussides form a family of porous molecular materials with relative wide diversity of crystalline structures and also of porous network topologies. These features make nitroprussides interesting cyanometallates-based materials where the role of structural factors on the hydrogen storage can be evaluated. The hydrogen adsorption was studied in $T[\text{Fe}(\text{CN})_5\text{NO}]$ with $T = \text{Mn, Fe, Co, Ni, Cu, Zn, and Cd}$; in a series of mixed compositions, $\text{Co}_{1-x}\text{T}_x[\text{Fe}(\text{CN})_5\text{NO}]$ with $T = \text{Mn, Fe, Ni, Zn, and Cd}$; and in $\text{Cu}_{0.55}\text{Ni}_{0.45}[\text{Fe}(\text{CN})_5\text{NO}]$. The largest hydrogen storage capacity was found for $\text{Ni}[\text{Fe}(\text{CN})_5\text{NO}]$, 2.54 mol/mol (1.85 wt %) at 75 K and 850 Torr. The hydrogen adsorption in nitroprussides shows a marked dependence on the properties of the metal (T) situated at the cavity surface. The electrostatic interaction between the hydrogen molecule quadrupole moment and the electric field gradient at the cavity surface appears to be the main driving force for the hydrogen adsorption, without discarding a possible direct interaction of H_2 with the metal (T). In structures with narrow channels (Mn, Cd), pronounced kinetic effects for the H_2 adsorption isotherms are observed, which were ascribed to a strong and localized interaction between the H_2 molecule and the metal at the cavity surface. The pore accessibility and the pore volume were evaluated from CO_2 adsorption isotherms. The free volume for all the compositions are accessible to the CO_2 molecule. The CO_2 stabilization within the cavities is also dominated by the electrostatic interaction. All the samples were previously characterized using X-ray energy-dispersed spectroscopy, X-ray diffraction, thermogravimetry, and infrared and Mössbauer spectroscopies.

1. Introduction

Nowadays, about 80% of the consumed energy comes from combustion of fossil fuels derivatives, energy source whose availability will be limited in the near future. The combustion of fossil fuels and their derivatives are also partially responsible for the emission of greenhouse gases and for the related global warming and climate changes. Among the alternatives to fossil fuels derivatives as energy sources, for use in automotive vehicles, for instance, combustion of hydrogen has been considered, due to its high caloric value (572 kJ/mol) and environmentally compatible byproduct (water).¹ Hydrogen has too low critical temperature (32.7 K) to be handled in liquid state for practical applications such as combustible. From these facts, a challenge for the development of a hydrogen-based energy technology is the availability of appropriate hydrogen storage media. The established target (2010 US DOE targets), in that sense, is 6 wt % for a reversible process and relatively short storage–release times.² To date, the highest hydrogen storage capacity in materials has been reported for chemical and metal hydrides,³ with some of them above that target.⁴ However, the desorption process of hydrogen stored as hydrides usually requires relatively high temperatures of heating (> 500 K) and this storage method is not always reversible.⁵ An

attractive option for a reversible process is the storage through physical adsorption in porous materials; however, to date, the reported gravimetric density of hydrogen adsorbed at atmospheric pressure remains below the target of 6 wt %, suggesting that more basic studies are required in order to increase the hydrogen storage density in porous solids. Several families of porous materials have been evaluated in that sense, among them, carbon-based solids,^{7,8} zeolites,^{9,10} and metal organic frameworks.^{11–13} More recently, porous coordination polymers, of Prussian blue type, have received certain attention as prototype materials for hydrogen storage;^{14–19} among them, cobalt and nickel nitroprussides have the highest reported hydrogen adsorption efficiency for a porous coordination polymer-based material, 1.68 wt %.¹⁷ Cobalt and nickel nitroprussides are only two members of this family of coordination compounds, which shows a relative wide diversity of crystalline structures and also of topologies for the porous network.²⁰ These features make nitroprussides an interesting family of porous molecular materials that deserves to be evaluated for hydrogen storage, particularly to obtain information on the role of the pore topology on the hydrogen adsorption. In addition, for the anhydrous phases of this family of compounds the assembling metal (T) is always found with an unsaturated coordination sphere and is located at the cavities' surface. As for the hydrogen interaction with such metal centers, a certain role for the H_2 adsorption in porous solids has been attributed.^{14–19,21}

In this contribution, the results obtained from a study on hydrogen storage in the family of transition metals nitroprussides, $T[\text{Fe}(\text{CN})_5\text{NO}]$ with $T = \text{Mn, Fe, Co, Ni, Cu, Zn, and Cd}$, including a series of mixed compositions,

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