

Materials for Hydrogen Storage: Use of the Pattern Background to Obtain Structural Information in Porous Solids

Rodriguez-Hernandez, J.,¹ Gómez A.,² and Reguera, E.¹

¹Universidad de la Havana - C. Havana Havan Cuba

²University of Guelph - Guelph ON Canada

INTRODUCTION

The adsorption in nanoporous solids is one of the alternatives that have been evaluated for the molecular hydrogen storage. The high density H₂ storage is probably the main challenge to be solved for the development of a hydrogen-based energetic technology to replace the use of fossil fuel derivatives in mobile applications. The option of storage in nanocavities is oriented to favor relatively strong H₂-surface interactions to allow the storage at temperature and pressure close to room conditions. The H₂-H₂ interactions that allows the hydrogen liquefaction are very weak and, in consequence, its critical temperature is relatively low (T_c = 32.9 K). Probably the paradigm for the hydrogen storage in porous solids is found in the coordination of the molecule to metal centers at the cavity surface [1]. It is well known that the surface atoms are always deviated from their ideal symmetry restricted positions, particularly when the coordination sphere remains unsaturated. This is the case of those metal centers of interest for hydrogen storage studies. Such deviation leads to certain incoherence for the dispersed radiation, resulting in broadening for the diffraction peaks and also increasing the patterns background. When heavy atoms are located at the materials surface, in the pattern background a sinuous contribution could be identified [2, 3], which can be used to obtain structural information on the true position of these metals. In this report this subject is discussed through the applications to the structural study of cubic Nitroprussides, T[Fe(CN)₅NO].xH₂O where T = Fe, Co, Ni. This series of compounds shows H₂ storage capacity without precedent for porous coordination polymers [4, 5].

EXPERIMENT

The materials to be studied were prepared and characterized according to already reported procedures [6]. High intensity XRD powder patterns of these samples were recorded at 10B-XPD beamline of the LNLS with $\lambda = 1.748098 \text{ \AA}$ (7.0877 keV), which is slightly above FeK absorption edge. XRD patterns were recorded at different temperatures in the 12-300 K range for both hydrated and anhydrous samples. The patterns of this series of porous solids show a sinuous feature, which was carefully fitted using the capability of the GSAS code for dealing with diffuse scattering [7]. To obtain the radial distribution function (RDF) of the pattern background, the peak contribution was removed and the resulting difference pattern

smoothed. From the calculated RDF the initial positions to be refined, for the metal centers were obtained. The refinement process was carried using GSAS code. At the end of the structure refinement the symmetry restrictions were ignored.

Table 1. Deviation δ (in \AA) of the metals from their ideal positions for T= Fe, Co

Sample	T (K)	$\langle\delta\rangle_{\text{Fe}}$	$\langle\delta\rangle_{\text{T}}$
FeNP.xH ₂ O	300	0.0119(6)	0.0095(6)
FeNP.0H ₂ O	300	0.0107(1)	0.0398(12)
FeNP.0H ₂ O	77	0.0107(1)	0.0415(12)
FeNP.0H ₂ O	12	0.0107(1)	0.0429(8)
CoNP.xH ₂ O	300	0.0124(9)	0.0103(9)
CoNP.0H ₂ O	300	0.0108(1)	0.0325(13)
CoNP.0H ₂ O	77	0.0108(1)	0.0336(12)
CoNP.0H ₂ O	12	0.0108(1)	0.0348(14)

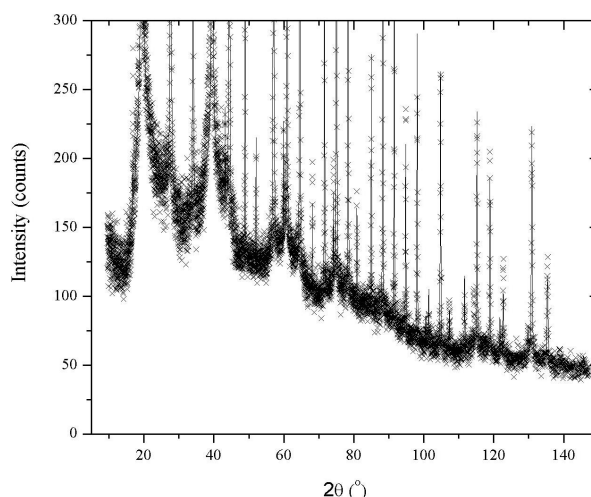


FIG. 1: Background for iron nitroprusside

RESULTS AND DISCUSSION

Figure 1 shows the sinuous background for iron nitroprusside. Figure 2 shows the calculated radial distribution functions (RDF) from the XRD pattern background for hydrated samples at room temperature. Indicated is assignment of the observed peaks. In Table 1 the calculated metal deviations from their ideal positions are reported. These deviations were