

Direct Synthesis of Mesoporous Carbon-Metal or Carbon-intermetallic nanoparticles used as Potential Absorbents for Hydrogen Storage.

Philippe Dibandjo¹, Claudia Zlotea², Roger Gadiou¹, Fermin Cuevas², Michel Latroche², Cathie Vix-Guterl¹

¹Institut de Sciences des Matériaux de Mulhouse (IS2M) LRC CNRS 7228, 15 Rue Jean Starcky, BP2488, F-68057 Mulhouse, France.

²Institut de Chimie et des Matériaux de Paris-Est, CNRS UMR 7182, 2-8, rue H. Dunant F-94320 Thiais, France.

Introduction

Recently, attention has been paid to porous carbons materials, owing to their large surface area, large pore, chemical inertness, and electrical conducting properties. In number of applications, such as adsorbents, catalyst supports, energy storage and conversion systems, is it essential to use micro and mesoporous carbons with well-tailored pore systems. For hydrogen storage application, these carbon materials have showed a low hydrogen storage capacity at ambient conditions [1,2]. One of the promising ways to increase hydrogen uptake at ambient conditions is to dope porous materials with transition metals [3]. The process used for the synthesis of the carbon containing metals nanoparticles is in two steps: (i) the synthesis of the porous carbon structure by the hard template route and (ii) liquid impregnation for the incorporation of metals in the porosity of the carbon host materials followed by the reduction treatment. This is a time-consuming and costly process.

In this work, we try to reduce the synthesis process into a one step process. To reach the goal, a soft-template approach was used. An ordered mesoporous (carbon-metal) or (carbon-intermetallic) were synthesized and characterized by TEM, XRD and nitrogen adsorption apparatus for their physical and chemical properties. Their hydrogen adsorption equilibria and kinetics at 77K and 298K was evaluated. The metal or intermetallic loadings were fixed to 10 wt%.

Experimental

A-Synthesis of ordered Mesoporous Carbon

The ordered mesoporous carbon was synthesized by the soft template approach following the procedures described in reference [4]. Resorcinol and phloroglycinol were completely dissolved in EtOH/water solution. HCl is introduced, and the solution was stirred for half an hour. Pluronic F127 was then added, and after it completes dissolution, formaldehyde was introduced. The solution was stirred for three days at ambient temperature, followed by filtration to separate the solid and the liquid. Then the solid was carbonized under argon up to 600°C for three hours.

B- In situ doping of ordered Mesoporous Carbon by Pd, Pd1-xNi.

In situ doping of metal or intermetallic into ordered mesoporous carbons was performed in a similar way as described above. For Pd precursor, a 10 wt% of an acid tetrachloropalladous solution in acetone was used and for Pd1-xNi, a solution of tetrachloropalladous acid, nickel nitrate and acetone was used. The precursor was added to the reaction mixture before the addition of formaldehyde and was kept stirring for half an hour, followed by the similar procedures adopted for the synthesis of ordered mesoporous carbon. The metal or intermetallic precursors were thermally cracked and become metal or intermetallic nanoparticles that were uniformly dispersed on the matrix during the carbonization procedure.

Results and Discussion

The TEM images of the carbon and Pd, Pd1-xNi doped carbons are shown in figure 1. It can be observed, small particles inside the carbon matrix. The particles are dispersed uniformly. The size of Pd clusters estimated by TEM is ranging between 2-6 nm and the size of Pd1-xNi clusters is between 6-20 nm.

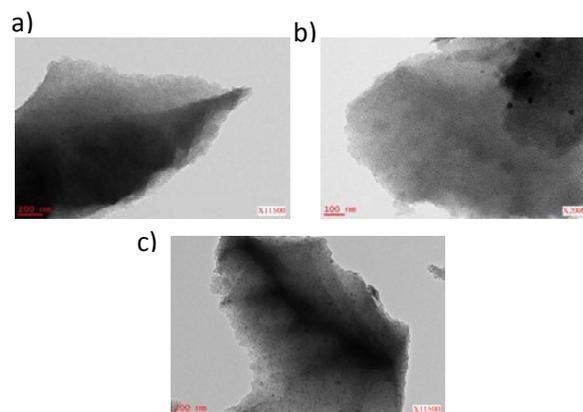


Figure 1: TEM images of a) pure carbon, b) C-Pd and c) C-Pd_{0.66}Ni_{0.34}.

The XRD patterns for the mesoporous carbons doped with Pd and Pd1-xNi are shown in figure 2. For both samples, the pattern displays five main broad peaks. The peaks at $2\theta = 23^\circ$, is common for the two samples and is attributed to the non-graphitized carbon, whereas the remaining four peaks can be indexed with the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections of a *fcc*-structure. For the C-Pd, the cell parameter is $a = 3.8907 \text{ \AA}$ which can be attributed to the Pd metallic particles. The C-Pd1-xNi displays a cell parameter of $a = 3.766 \text{ \AA}$. This value lies between those of Pd ($a = 3.8907 \text{ \AA}$) and Ni ($a = 3.524 \text{ \AA}$) confirming the formation of an alloy. By using these parameters we calculated the x the value to be $x = 0.34$.

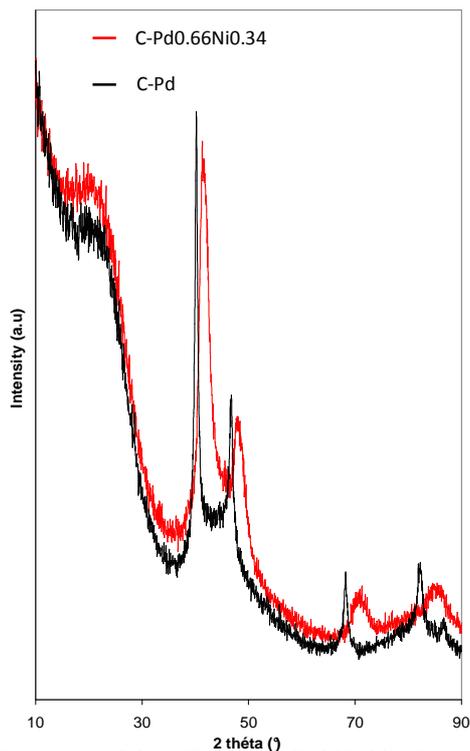


Figure2: XRD of C-Pd and C-Pd0.66Ni0.34.

Nitrogen adsorption and desorption isotherms at 77 K were measured to characterize the textural properties of the three samples.

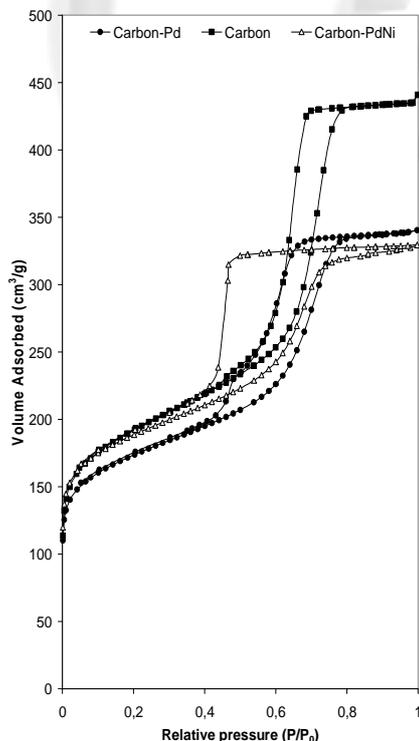


Figure3: Nitrogen adsorption-desorption of (▪) Pure carbon, (•) C-Pd and (▲) C-Pd0.66Ni0.34 materials.

The adsorption data are summarized in table 1.

Samples	S_{BET} (m^2/g)	V_P (cm^3/g)	V_{DR} (cm^3/g)	D_p (nm)
Pure Carbon	635	0.68	0.27	6.2
C-Pd	570	0.52	0.29	5.4
C-Pd0.66Ni0.34	615	0.51	0.27	4.8

S_{BET} : Specific surface area; V_P : Total pore volume P/P_0 : 0.99; V_{DR} : Microporous pore volume estimated by Dubinin method; D_p : Pore diameter using adsorption branch.

The isotherms are shown in Figure 3. They display a type IV slope characteristics of mesoporous materials with a hysteresis loop. The introduction of Pd or Pd0.66Ni0.34 during the synthesis slightly changes the textural properties of the pure mesoporous carbon materials (table1). It is observed that nitrogen uptake as well as BET specific surface area decrease with the metal loadings. The decrease of the pore volume as well as the pore diameter is probably due to the dispersion of metal particles inside the pores and matrices of the carbon. It is also possible that the addition of metal precursors has changed the nature of the polymer solution and generated slightly different pore texture during the carbonization process.

Conclusions

By using the soft template route, it was possible to synthesize metal or intermetallic doped porous carbon. The materials obtained by this way presented a uniform dispersion of the nanoparticles in the matrix of the carbon materials. It was also possible to obtain nanometric Pd or Pd0.66Ni0.34 clusters during the synthesis.

Acknowledgment. The Centre National de la Recherche Scientifique (CNRS) is gratefully acknowledged for the financial support through the PAN-H program (ANR MATHYSSE).

References

- [1] Gadiou, R; Saadallah, S. E; Piquero, T; David, P; Parmentier, J; Vix-Guterl, C; Microporous and Mesoporous Mater. 2005, 79,121.
- [2] Xia, K; Gao, Q; Wu, C; Song, S; Ruan, M; Carbon 2007, 45, 1989.
- [3] Wang L and Yang RT, Energy & Environ. Sci. 2008, 1, 268.
- [4] Tanaka, S; Doi, A; Nakatani, N; Katayama, Y; Miyake, Y; Carbon 47 (2009) 2688.