

Influence of the Thermal Reduction Process on the Size of Pd Nanoparticles during the Space Confined Synthesis inside Mesoporous Carbons Materials.

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Introduction

Nanometer-size materials are of great interest for fundamental research and technical applications due to their size and shape dependent properties and excellent chemical processibility [1]. Extensive academic and industrial efforts are focused on the research about nanoclusters due to their potential applications in fields such as catalysis, solar cells and hydrogen storage [2,3]. Especially hybrid materials constituted of nanosized metal embedded into porous carbon gained recently of interest as hydrogen storage medium. These materials show highest hydrogen storage capacity at room temperature compared to each material separately [4]. However, they are still open questions among them the effect of the size of the metal nanoparticle on the hydrogen capacity and the influence of the surface properties of the host mesoporous carbon materials on the metal nanoparticle size.

In other to answer to those questions, C/Pd hybrid materials starting from two mesoporous carbon materials having different surface properties were synthesized. The nanoclusters of Pd were formed inside the carbon porosity by impregnation of the carbon by a palladium salt followed by a thermal reduction of the salt. Different reduction processes were applied. The characteristics of the as-synthesized hybrid materials as well as their hydrogen storage capacity were studied in relation with the size of the Pd nanoparticles, the nature of the mesoporous carbon used and the experimental conditions of the thermal reduction.

Experimental

The carbon was prepared by templating of SBA-15 silica [5-7]. The SBA-15 was synthesized according to the procedure described in the literature [8]. The temperature used for the silica synthesis was 373K. The obtained silica displays cylindrical pores with a diameter close to 5 nm and a mean wall width around 4 nm. The carbon was introduced into the SBA-15 porosity by two ways:

(1) Chemical vapor deposition (CVD) of propylene at 1023K. The CVD was done with a flow of 3% volume of propylene in argon. The carbon material obtained by this route is noted (CT_P).

(2) Liquid phase infiltration of sucrose followed by calcination under vacuum at 1173K. The carbon material is named (CT_S).

Then, to recover the carbon material, the mixed material (silica/carbon) was stirred for 4 hours in a HF solution (40% volume concentration) to remove the silica template. The solution is further filtered and washed with distilled water and finally dried overnight in an oven at 353K.

In order to disperse Pd nanoparticles into the carbon template, a procedure close to the one described by Joo et al. was performed [9]. A solution of acid tetrachloropalladic (H₂PdCl₄, Pd 10 wt.%) was prepared by dropping 0.3353 g of PdCl₂ (Alfa Aesar, purity 99.9%) into 10 ml of 10 vol% HCl aqueous solution under stirring at 35°C until complete dissolution. The carbon (0.5 g) was impregnated with 2.5 ml of an acid tetrachloropalladic solution in acetone (5 ml), stirred for several hours and dried under air at 333K. Next, PdCl₄²⁻ ions were reduced by three different reduction routes:

(I) the impregnated carbon template was heating in an argon flow (0.6 l/h) at 773 K for 6 h. The as-synthesized samples were named CTs-773-Pd and CTp-773-Pd.

(II) The impregnated carbon template was heating in an Ar/H₂ flow (0.5 l.min⁻¹) at 573 K for 6 hours. The sample was then outgassed under secondary vacuum for 11 hours at 573 K. The as-synthesized materials were named CTs-573-Pd and CTp-573-Pd.

(III) The impregnated carbon was submitted to a plasma treatment under argon at room temperature. The sample was put on a silica glass support and placed in the glow discharge cell. The argon pressure was adjusted to 1 mbar; the glow discharge plasma was generated by applying a power of 100 watts for 30 min. The as-synthesized samples were named CTs-298-Pd and CTp-298-Pd.

Results and Discussion

Chemical analysis obtained by ICP-OES and thermogravimetric analysis (TGA) confirmed that the Pd content in each sample corresponds to the nominal composition of the starting solution used for impregnation (10wt% of Pd). The particles size of each sample estimated by XRD and TEM are gathered in Table 1

Table1: Pd average size.

Samples	Thermal reduction process	Pd average size (nm) Scherrer/TEM	Onset oxidation temperature (°C)
CTs	-	-	470
CTp	-	-	510
CTs-773-Pd	Ar	13.9 / 15	410
CTs-573-Pd	Ar/H ₂	2.5 / 2.6	320
CTp-773-Pd	Ar	8.9 / 11.1	460
CTp-573-Pd	Ar/H ₂	2.5 / 2.8	340
CTp-298-Pd	Plasma	- / ≤ 2	420
CTs-298-Pd	Plasma	- / ≤ 2	400

It can be observed by TGA under air that the oxidation for the Pd-containing carbons starts at a temperature lower than the temperature of the corresponding carbon host and that depends on the Pd particle size. This is observed whatever the type of carbon hosts used (CTp or CTs).

The TEM images (Figure 1) and the textural characterizations (specific surface area, total pore volume, microporous volume determined by nitrogen adsorption) indicate that the presence of the palladium nanoparticles only slightly modifies the characteristics of the ordered carbons. These results confirm that it is possible to use ordered porous carbon as nano-reactors for the synthesis of metal nanoparticles without any significant modification of the carbon porous organization.

Pd with different particle size could be obtained by using different reduction routes and carbon templates (CTp or CTs). The reduction of the palladium salt by the argon/H₂ process at a temperature of 573 K allows synthesizing small Pd nanoparticles independently on the nature of the carbon host. In the case of the reduction carried out at 773 K, it could be noted that the final particle size also depends on the carbon template used. The particle size is lower if the Pd was prepared into a carbon originated from propylene compared to the carbon issued from sucrose. The difference of the surface chemistry between these both carbons could be at the origin of this phenomenon.

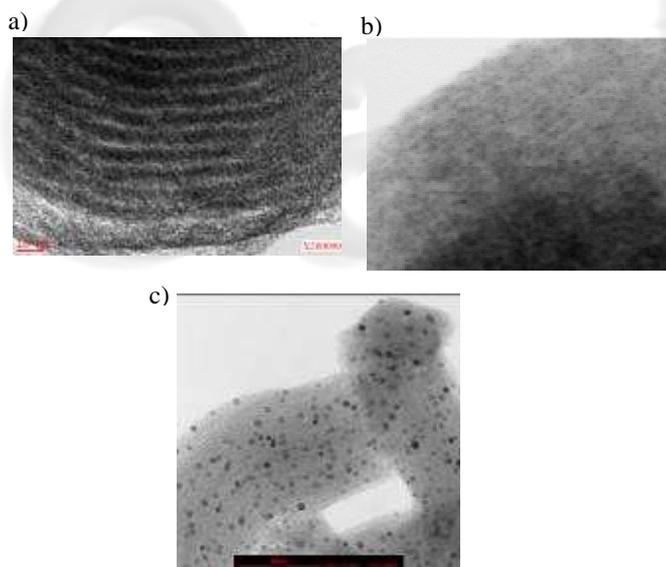


Figure 1: TEM images of a) CTs-298-Pd, b) CTs-573-Pd and c) CTs-773-Pd.

The hydrogen sorption was tested for the as-pristine carbons and the Pd-containing carbons at 298K. In all cases, the hydrogen storage capacity is higher for the C/Pd samples compared to the carbon samples while the surface area and the micropore volume per g of carbon of these samples are lower compared to the carbon sample (For CTs is 0.3wt% and for Cts-573-Pd is 0.37wt% at 4MPa).

The enhancement in hydrogen storage was mainly due to the presence of Pd nanoparticles, which allowed the spillover of atomic hydrogen from metal particles to carbon host matrix.

One important issue of this study was the effect of the Pd nanoparticles size on the hydrogen adsorption. As an example, the Pd particle size is different in the CTp-773-Pd and CTp-573-Pd samples obtained from the same carbon template. A significant increase of the sorption capacity was measured for the sample having a smaller particles size (CTp-573-Pd) from 0.19 wt% to 0.27 wt% at 4MPa.

Conclusions

The use of different carbon source and different thermal reduction routes allows us to synthesized C/Pd materials with various Pd nanoparticles size. The palladium was homogeneously dispersed into the porosity of the carbon template porosity. The textural properties of the carbon materials were not significantly modified by the presence of the Pd nanoparticles. The plasma reduction process leads to the formation of the smallest Pd nanoparticles independently from the nature of the carbon host materials. At room temperature, it seems that hybrid materials with small Pd nanoparticles size display higher H₂ storage capacity.

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