

# HYDROGEN ADSORPTION IN ORDERED MESOPOROUS CARBONS DOPED WITH Pd, Pt, Ru AND Ni

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## Introduction

Hydrogen fuel cells are one of the most promising power sources for future transport systems. However, hydrogen storage is the bottleneck of this new technology. Hydrogen can be stored as compressed gas, as liquid, or through chemical or physical adsorption. Among the many physical adsorbent materials evaluated for hydrogen storage, none of them can meet the DOE target due to a low hydrogen adsorption capacity at ambient temperature [1].

It is believed that porous materials doped with palladium, platinum, ruthenium or nickel can adsorb more hydrogen through the spill-over effects [2]. The ordered mesoporous carbon (OMC) is a unique porous carbon material that was first prepared by Ryoo et al [3] using the hard-template method. In the hard-template method, a carbon precursor is coated on a mesoporous silica template, then carbonized at high temperature, following with removal of the template to form the mesoporous carbon. The soft-template method developed by Dai et al [4] is relatively new and unique as compared with the hard-template method. In this particular process, one single polymer or the carbon precursor is prepared, part of which is used as the templating agent and the remaining portion is used as the carbonization agent, thereby not requiring any template removal process used in the hard-template method.

We explored the feasibility of increasing hydrogen adsorption by doping different transition metals on porous carbon. The ordered mesoporous carbon was synthesized using the soft-template and doped with 1 wt.%, 5 wt.% and 10wt.% of one of the metals (palladium, platinum, nickel and ruthenium). All adsorbents were characterized for their pore textural properties by nitrogen adsorption, their morphology by TEM and phase structure by the XRD analysis. Hydrogen adsorption and desorption properties on these adsorbents were also measured at both ambient pressure and elevated at room temperature. The hydrogen spill-over effect was analyzed by comparing the hydrogen adsorption on the doped and virgin carbons.

## Experimental

### Material Synthesis

The ordered mesoporous carbon samples were synthesized by the soft-template approach following the procedures developed by Dai's group [4]. 1.25 g of Phloroglucinol and 1.25 g of F127 were dissolved in 4.26 g of deionized water and 4.76 g of 99.9% ethanol. Then 5 drops of 37% hydrochloric acid were added to the solution as catalyst. The

resulted solution was stirred for 30 minutes until light pink color appeared in the solution. 1.3 g of 37% formaldehyde were then added and the solution became cloudy after 30 minutes of stirring. After stirring of about another hour the mixture was allowed to settle for 15 minutes. The bottom layer of the mixture contained the polymer solution and upper layer was basically composed of ethanol-water mixture. The bottom layer separated from the mixture was then carbonized in a furnace at temperature up to 850 °C.

In-situ doping of transition metals were performed in the process of synthesizing the carbons. Metal acetylacetonate of each of the metals, abbreviated as Pd(acac)<sub>2</sub>, Pt(acac)<sub>2</sub>, Ni(acac)<sub>2</sub> and Ru(acac)<sub>3</sub> were selected as the precursors. Given amounts of metal acetylacetonates were added to reaction mixture after the 30 minutes of addition of HCl (when the reaction mixture becomes light pink) and stirred for 10 minutes. 1.3 g of 37% formaldehyde were then added to the reaction mixture followed by the similar procedures adopted for the synthesis of pure ordered mesoporous carbons. The metal acetylacetonates were thermally cracked giving rise nanoparticles of the metals inside the carbon matrix during the carbonization procedure. About 1%, 5% and 10% of each of the metals were doped to the carbons.

### Materials Characterization

The Hitachi H7650 transmission electron microscope was used to examine the materials structure and presence of metal nanoparticles, the Rigaku<sup>®</sup> Miniflex-II X-ray diffractometer with a zero-background sample holder was used to study the phase structure of the doped carbon samples, and nitrogen adsorption at 77K was performed to measure the pore structural properties of the carbon adsorbents in a Micromeritics<sup>®</sup> ASAP 2020 apparatus.

### Hydrogen Adsorption

Hydrogen adsorption equilibrium and kinetics on the carbon adsorbents at ambient temperature and pressure up to 1 bar were measured volumetrically in the Micromeritics<sup>®</sup> ASAP 2020 adsorption apparatus. High pressure adsorption was performed gravimetrically in a magnetic suspension balance (Rubotherm) at room temperature and pressure up to 300 bar. This balance is equipped with an automatic gas dosing and pressure control system, and a booster pump for increasing the hydrogen pressure.

## Results and Discussion

The nitrogen adsorption and desorption isotherms measured at 77K were used to calculate the specific surface area, pore size distribution and pore volume for all the carbon

adsorbents. Figure 1 is an example of nitrogen adsorption and desorption isotherms (1(a)) and corresponding pore size distributions (1(b)) for the Ni-doped carbon adsorbents. The nitrogen adsorption/desorption isotherms are of type IV, the desorption hysteresis suggests the mesoporous structure of the carbon adsorbents. It can be observed from Figure 1 that the Ni doping amount strongly affects the pore textural properties of the ordered mesoporous carbon. A high doping amount leads to a lower nitrogen adsorption amount and smaller median pore size.

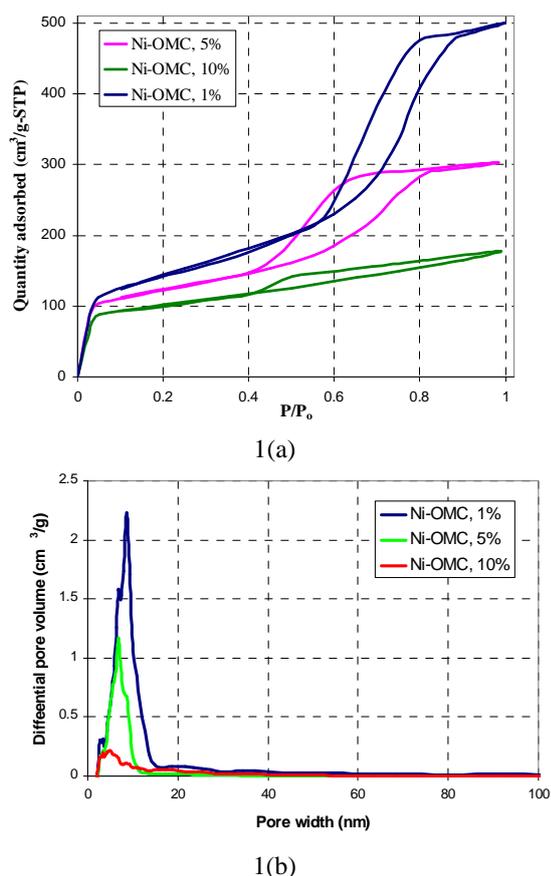


Figure 1. N<sub>2</sub> Adsorption and desorption isotherms at 77K (a) and corresponding pore size distributions for the Ni-doped ordered mesoporous carbon adsorbents (b).

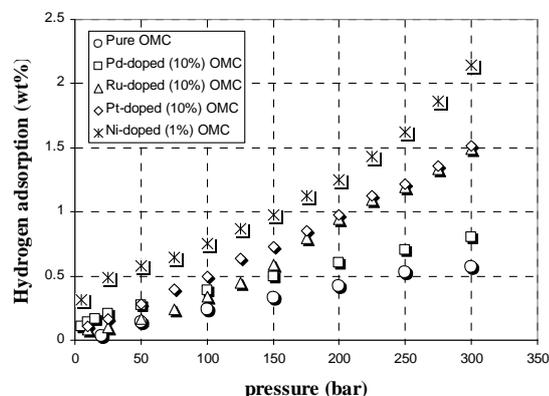


Figure 2. Hydrogen adsorption isotherms on Pt-, Pd-, Ru- and Ni-doped ordered mesoporous carbon at 297 K

Table 1 summarizes the pore textural properties and the hydrogen adsorption capacities for all the carbon adsorbents investigated in this work. Figure 2 compares the hydrogen adsorption isotherms on all the carbon adsorbents at ambient temperature (297K) and hydrogen pressures up to 300 bar. As shown in Figure 1, the metal-doped carbon adsorbents have a higher hydrogen adsorption capacity than that of the pure ordered mesoporous carbon. The results shown in Table 1 suggest that the hydrogen adsorption amount is affected by the metal doping amount. Except for the Ni-doped carbons, higher metal doping amounts lead to higher hydrogen adsorption capacities. The Ni-doped carbons show a very different behavior. The carbon doped with 1 wt.% of Ni has the highest hydrogen adsorption, and the hydrogen adsorption amount decreases with Ni amount. It is interesting to observe that the highest hydrogen adsorption amount of 2.15% was obtained on the 1 wt.% Ni-doped carbon adsorbent.

Table 1. Summary of physical properties and hydrogen adsorption capacities of the metal-doped carbons

Metal	Doping amount (wt.%)	BET (m <sup>2</sup> /g)	H <sub>2</sub> uptake at 1 bar (wt.%)	H <sub>2</sub> uptake at 300 bar (wt.%)
Pd	1%	483	0.064	
	5%	400	0.077	
	10%	342	0.083	0.80
Pt	1%	513	0.069	
	5%	507	0.095	
	10%	346	0.099	1.50
Ni	1%	495	0.130	2.15
	5%	397	0.093	
	10%	321	0.083	
Ru	1%	423	0.070	
	5%	495	0.076	
	10%	435	0.077	1.49

## Conclusion

1. Doping the ordered mesoporous carbons with transition metals can increase hydrogen adsorption capacity.
2. Ordered mesoporous carbon doped with 1 wt.% nickel can adsorb 2.15 wt.% hydrogen at 297K and 300 bar.

## Acknowledgement

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