

Palladium-doped Carbon Porous Materials as Adsorbents for Hydrogen Storage

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Abstract

Hydrogen has been recognized as an ideal energy carrier because it is clean and easy to produce from renewable energy sources. In the past several decades, efficient hydrogen storage and transport devices have been the major concerns in hydrogen-energy technology. H₂ storage schemes in terms of compressed or liquefied gas are undesirable due to low storage density and high cost. Recently, carbon porous materials (CPMs) with well-defined pore structures offered great potential as adsorbents for H₂ storage. Several existing literature reports revealed that, when doped with transitional-metals (such as Pt, Pd, Ni etc.), carbon-based adsorbents exhibit enhanced H₂ uptake due to spillover effect. This study aims to compare the effects of doping palladium (Pd) on H₂ storage properties of various carbon materials, including ordered mesoporous carbons such as FDU-15, CMK-3, and CMK-5, as well as activated carbon (AC) and activated carbon fiber (ACF). Two metal doping routes, namely post-synthesis impregnation and one-pot synthesis methods were implemented and compared. Typically, carbon adsorbents so synthesized with varied Pd loadings were first subject to evacuation treatment prior to H₂ uptake measurement (pressure: 7 bar; RT). Our preliminary results show that Pd/C materials prepared by either methods exhibit higher H₂ storage capacity compared to their pristine counterparts, which

have BET surface area following the order: ACF (1546 m²/g) > CMK-5 (1341) > CMK-3 (1024) > AC (1038) > FDU-15 (794). Compared to Pd/C prepared by one-pot synthesis method with a similar Pd loading of 8 wt%, those fabricated by post-synthesis impregnation appear to be more effective in terms of their H₂ storage capacities, which obey the trend: Pd/CMK-5 (0.57 wt%) > Pd/ACF (0.50) > Pd/AC (0.46) > Pd/CMK-3 (0.41) > Pd/FDU-15 (0.30). Among them, Pd/CMK-5 prepared by post-synthesis impregnation method showed the best H₂ uptake capacity of 0.57 wt%. This is attributed to the better dispersed Pd metal particles in Pd/C adsorbents prepared by post-synthesis impregnation method than direct synthesis route, as verified by results obtained from TEM measurements. The effect of Pd loading on H₂ uptake phenomena will also be discussed.

Keywords: Hydrogen storage; Porous carbons; Impregnation, One-pot synthesis, Pd

1 Introduction

氫氣被公認為一種理想的能源氣體，因他是環保且容易再生的，過去除青技術大多採用液態氫作為壓縮存儲的方式，所以不是和廣泛使用，因為存儲密度低、成本高也較危險，近年來則是採用一些多孔性材料做物理或化學吸附氫氣，其中碳材被證實具有相對較高的儲氫量、

重量輕且成本低，另一項重點是碳材與附載過渡金屬增加氫吸附量方法。通過加載的金屬，金屬離解氫分子之後氫被吸附，鈀附載碳材的儲氫能力被認為是大於原來樣本30%的效果。

2 General Instructions

本研究中以碳為基材，將活性金屬鈀以含浸法及一步合成法參雜到碳基材上，含浸法包括CMK-5、FDU-15、市售活性碳及碳纖維之比較，一步合成則為CMK-5及FDU-15之比較。CMK-5是以傳統方式合成的SBA-15當作硬模板，以Furfuryl alcohol 和 Trimethyl benzene 當作碳源，經過熱處理及碳化後製得。FDU-15是以甲醛及苯酚做碳源，去做一個有機自組裝的反應，在透過錶面活性劑可形成一有序中孔碳材，如圖1。上述兩碳基材是以Palladium acetylacetonate為金屬源。

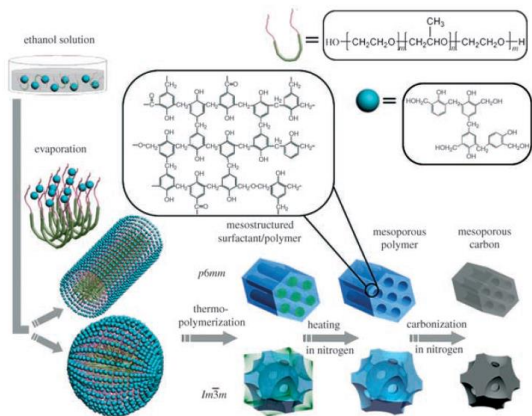


Figure 1. Schematic representation of the procedure used to prepare mesoporous polymers and carbon frameworks.

圖1

含浸法的製備方式是以各置備好的碳基材和金屬源PdCl₂混和，再使用過量的NaBH₄來還原鈀金屬，乾燥後可制得各樣品。

將兩系列製備好之樣品做基礎鑑定，包括:BET、XRD、TEM、TGA、TPD以及氫吸附測試。本實驗吸附裝置如附圖2。

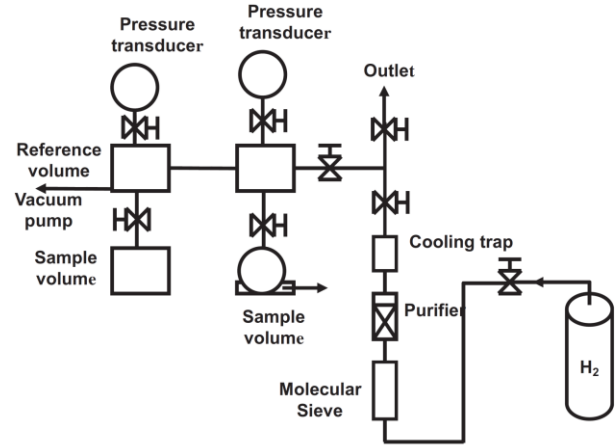


圖2

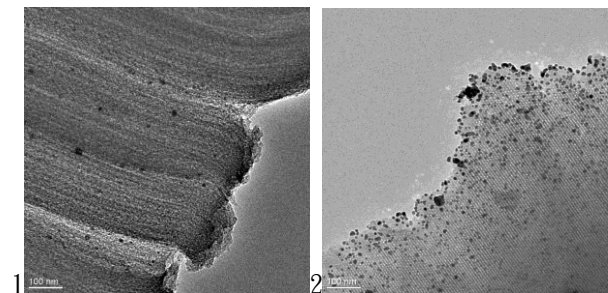
3 Results and discussion

表一為各樣品之BET結果，顯示出各樣品均有高的表面積與孔體積。

Sample	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
CMK-5	1341	1.1	3.2
FDU-15	794	0.9	4.6
AC	1038	1.0	0.2
CF	1546	1.0	0.2
Pd/CMK-5-O	1301	1.0	2.9
Pd/FDU-15-O	724	0.4	3.6
Pd/CMK-5-I	1288	1.3	2.8
Pd/FDU-15-I	692	0.4	3.3
Pd/AC-I	972	0.6	0.2
Pd/CF-I	1438	0.8	0.2

表一

TEM結果顯示含浸法製備的CMK-5和FDU-15樣品，均有一量好的有序孔道及金屬分散，金屬粒子大小約為7-8 nm左右，如附圖3。一步合成之樣品，同樣呈現出量好的有序孔道，但金屬粒子有聚集的狀況，大小約為20 nm左右，我們認為是因為在一步合成加熱聚合時，Pd尚未與碳源完全交合，造成在升溫時產生的聚集現象。如附圖4。



1

2

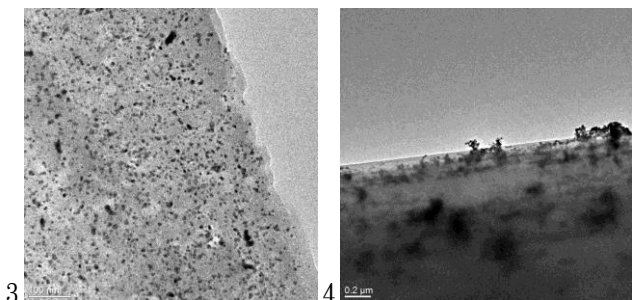


圖3

(1. Pd/CMK-5-Imp, 2. Pd/FDU-15-Imp, 3. Pd/AC-Imp, 4. Pd/CF-Imp)

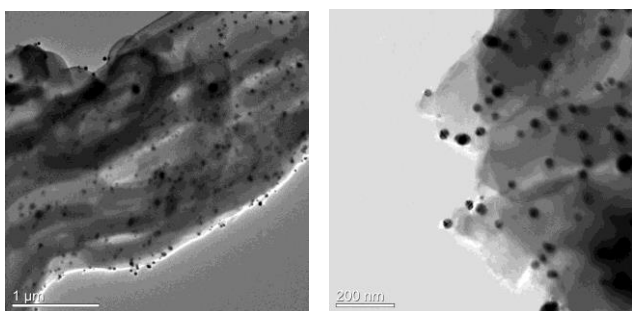
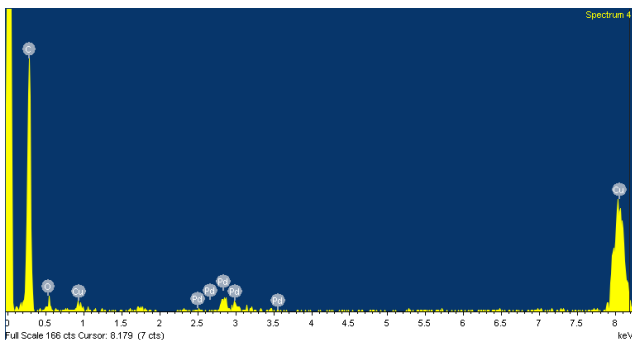
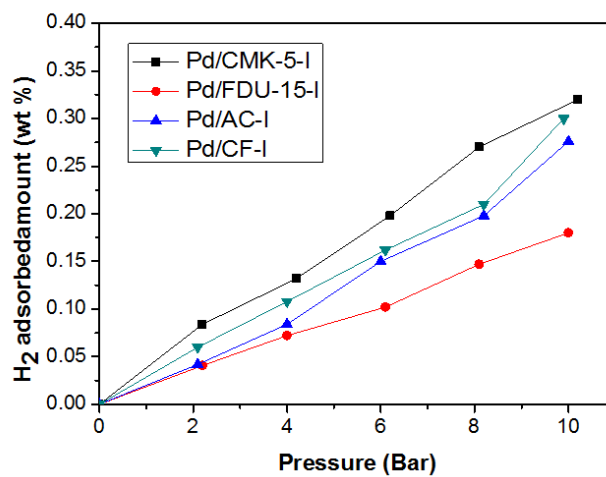
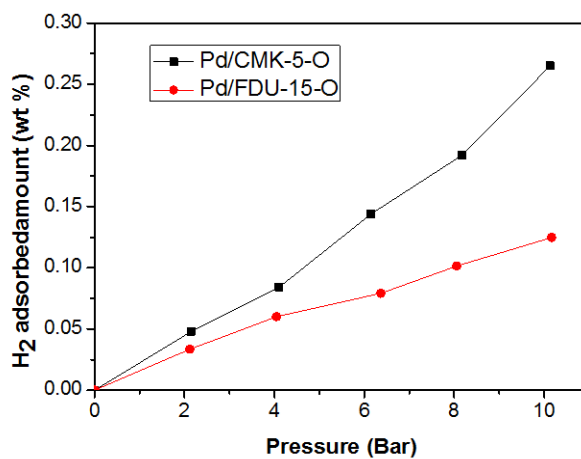


圖4(Pd/CMK-5-One Pot)



氫吸附測試於室溫、壓力到達10 Bar，個系列均已CMK-5 樣品有一最大吸附量，我們認為是因其高的表面積以及小的金屬粒子，及良好的分散性。如附圖5。



圖

4 Conclusion

本研究使用一步合成及含浸法混合碳材及鈀金屬，除氫測試在室溫下壓力到10 Bar，結果表明，經過Pd修飾的氫吸附能力增加了25%的效果，主要原因是因為Pd增加了材料表面的氫溢流現象，證明碳載體混合Pd在儲氫上是可行且具有應用潛力的材料，未來將針對一步合成的合成方式，如何降低金屬粒徑大小等課題做進一步的探討及研究。

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