HYDROGEN ADSORPTION ON PLATINUM DOPED ACTIVATED CARBON

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

MARCH 2017

To my dearest:

Baba Mama

Family

Late MakCu and Mak Uda(Alfatihah)

Supervisors

Friends

ACKNOWLEDGEMENT

Firstly, I would like to express my sincere gratitude to my supervisor, Assoc. Prof Adnan Ripin and co-supervisor, Dr. Tuan Amran Tuan Abdullah for the continuous support and courage of my master study and related research, for their patience, motivation, and immense knowledge. They have inspired me to become an independent researcher and helped me realize the power of critical reasoning. Through their guidance helped me in all the time research and writing of this thesis.

I am very grateful to all people I have met along the way and have contributed to the development of my research including lab assistant/ technician especially En. Rafiza and En. Shairray. In particular I would thank my fellow labmates (Ashikin, Wong, Afizah) for the days we were working together and all the fun we had in the last three years.

Last but not the least, I would like to thank my family: my parents, my sisters and brother for supporting me spiritually throughout writing this thesis and my life in general. The experiences that I obtained through this journey will be remembered for the rest of my life. Thank you very much.

ABSTRACT

Hydrogen energy system is expected to progressively replace the existing fossil fuels in the future. In particular, one potential use of hydrogen lies in powering zero-emission vehicles via a proton exchange membrane fuel cell (PEMFC). However, to make the PEMFC works on a vehicle, hydrogen storage is one of the critical components. When hydrogen is used on the vehicle, the equipment must has a high storage capacity. Carbon with high porosity and surface area as well as with the presence of metal loading were expected to obtain the maximum hydrogen adsorption via spillover effect on activated carbon (AC). The main objective of this research is to investigate the hydrogen adsorption on AC and platinum (Pt)-doped AC samples with different pressures (150, 250 and 350 psig). A comparative characterization was carried out using field emission scanning electron microscopy, x-ray diffraction and nitrogen adsorption isotherm analysis. It was shown that the presence of Pt metal reduced the surface area of AC from 675.32 $m^2.g^{-1}$ to 638.65 $m^2.g^{-1}$. Hydrogen adsorption at 150, 250 and 350 psig at room temperature exhibited two distinct behaviours. At 150 psig, the textural properties are critical and the adsorption capacities slightly increased with the Pt loading. On the contrary, at the higher pressure, the contribution of Pt nanoparticles was positive and marked by increased amounts of hydrogen reversibly adsorb from 0.7 to 0.9 wt.%. However, the amount of hydrogen uptake for Pt-doped AC was slightly lower compared to AC. AC adsorbed 1.07 wt.% of hydrogen at 350 psig compared to 0.9 wt.% for 10 wt.% Pt-doped AC. These findings have significant implications for the hydrogen storage in carbon-based materials, and further study needs to be done to enhance hydrogen uptake for Pt-doped AC.

ABSTRAK

Sistem tenaga hidrogen dijangka bakal menggantikan bahan api fosil sedia ada pada masa akan datang. Khususnya, hidrogen berpotensi untuk menjana kenderaan dengan pembebasan sifar melalui sel bahan api pertukaran proton membran (PEMFC). Walau bagaimanapun, untuk menggunakan PEMFC pada kenderaan, penyimpan hidrogen adalah salah satu komponen yang kritikal. Apabila menggunakan hidrogen pada kenderaan, peralatan mestilah mempunyai kapasiti penyimpanan yang tinggi. Karbon dengan keliangan dan luas permukaan yang tinggi serta kehadiran muatan logam dijangka mencapai penjerapan hidrogen yang maksimum melalui kesan limpahan ke atas karbon teraktif (AC). Objektif utama kajian ini adalah untuk mengkaji penjerapan hidrogen pada sampel AC dan AC berdop platinum (Pt), dengan tekanan yang berbeza (150, 250 dan 350 psig). Perbandingan pencirian telah dijalankan menggunakan mikroskop elektron pengimbas pancaran medan, pembelauan sinar-x dan analisis isoterma penjerapan nitrogen. Adalah ditunjukkan kehadiran logam Pt mengurangkan luas permukaan karbon teraktif daripada 675.32 $m^2.g^{-1}$ ke 638.65 $m^2.g^{-1}$. Penjerapan hidrogen pada 150, 250 dan 350 psig di suhu bilik menunjukkan dua kelakuan berbeza. Pada tekanan 150 psig, sifat-sifat tekstur adalah kritikal dan kapasiti penjerapan meningkat sedikit dengan muatan Pt. Sebaliknya, pada tekanan yang lebih tinggi, sumbangan partikel nano Pt adalah positif dan ditunjukkan dengan penambahan jumlah hidrogen terjerap berbalik iaitu daripada 0.7 ke 0.9 wt.%. Walau bagaimanapun, jumlah pengambilan hidrogen untuk AC berdop Pt adalah rendah berbanding dengan AC. AC menjerap 1.07 wt.% hidrogen pada 350 psig berbanding 0.9 wt.% untuk 10 wt.% AC berdop Pt. Hasil kajian ini mempunyai implikasi yang besar untuk penyimpanan hidrogen dalam bahan yang berasaskan karbon, dan kajian lanjut perlu dilakukan untuk meningkatkan pengambilan hidrogen untuk AC berdop Pt.

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LIST OF ABBREVIATIONS AND SYMBOLS

AC - Activated Carbon
BET - Breuner-Emmer and Teller
CNT - Carbon Nanotube
CVD - Chemical Vapour Deposition
DOE - Department of Energy
EDX - Energy Dispersive X-ray
EFB - Empty Fruit Bunch
FESEM - Field Emission Scanning Electron
GHG - Greenhouse Gas
GNF - Graphite Nanofiber
INS - Inelastic Neutron Scattering
IUPAC - International Union of Pure and Applied Chemistry
MOF - Metal Organic Framework
PEM - Polymer Electrolyte Membrane
RM - Ringgit Malaysia
R&D - Research and Development
SOE - Solid Oxide Electrolyzer
TC - Template Carbon
TCD - Thermal Conductivity Detector
TPR - Temperature Programmed Reduction
XRD - X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Storage of hydrogen has attracted worldwide attention because of the demand for a clean and efficient energy. Basically, the hydrogen storage implies the reduction of a large volume of hydrogen gas. In order to increase the density of hydrogen in the storage system, the hydrogen must either be liquefied or compressed at low temperature and high pressure (Eberle *et al.*, 2009). Previous studies in hydrogen storage found that repulsion has to be reduced, and it can be done by interactions of hydrogen with materials such as Ti-doped $NaAlH_4$ (Bogdanović &Schwickardi, 1997), metal hydrides (Sakintuna *et al.*, 2007), and complex hydrides (Eberle *et al.*, 2006). Even though these systems have reasonable volumetric capacities and irreversible, the systems are highly gravimetric. The reversible complex metal hydrides are facing challenge to meet the gravimetric target, which is limited to lightweight elements (Stetson & Petrovic, 2009). A promising storage method focused on porous materials such as carbon-based, zeolites, and metal organic frameworks (MOFs) through the adsorption process.

Adsorption process demands for a highly porous material to allow for easy uptake and release of hydrogen. Characteristics of activated carbon such as high density of adsorbent phase, high surface area, and abundant pore volume has been proved as one of the promising adsorbent for the hydrogen in future (Jin *et al*., 2007). However, interaction of Van de Wall forces and hydrogen adsorption towards the adsorbent surface is weak. Thus, one possible way to satisfy the hydrogen storage requirements using activated carbon is to dope the metal onto activated carbon, the spillover effects help the hydrogen to act as the storage medium (Konda & Chen, 2016). Transition metals such as Pt, Pd, Ni, and Ru are the most metal that researcher used to study the mechanism of hydrogen storage on metal doped activated carbon. Tsao *et al*., (2010) has successfully proved the increasing of adsorption percentage by the spillover effect of Pt metal.

1.2 Problem Statement

The search for a long-term hydrogen storage material in future is an urgent issue to be addressed by hydrogen-powered society. Several technical suggestions are anticipated to solve the storage issue, including compression or liquefaction of hydrogen gas, storage in metallic hydrides, chemical storage, and hydrogen storage by physisorption (Leon, 2008). However, liquefaction requires high amount of energy (Eberle *et al*., 2009), compression must be operated at very high pressure, and metallic hydrides are suspected to be poisonous while having incomplete reversibility and low kinetics behaviour (Murray *et al*., 2009). These drawbacks may lead to higher operation cost (Klell, 2010) and/or safety issues. Meanwhile, physisorption storage system on carbon materials is an interesting alternative. This is because it operates at low pressure, and is completely reversible with fast kinetics. Moreover, it relatively offers higher hydrogen storage capacity.

Adsorption storage on nanostructured material such as carbon may offer advantages compared to other materials by providing a high surface area and low density. By having high porosity and surface area, carbon provides high ratio of binding sites in the pores and on the surface to its weight, and thus increase the storage. Increasing hydrogen uptake by spillover in porous materials including nanostructured carbons, zeolites, and MOFs, have been developed by many researchers (Li & Yang, 2006; Li & Yang, 2007; Chen & Yang, 2010; Wang *et al.*, 2010; Chen *et al*., 2012). A wide range of metal loadings were considered in attempts to obtain the maximum hydrogen adsorption via spill over (Takagi *et al.,* 2004; Anson *et al.,* 2007) and large proportion of the increase in hydrogen adsorption is contributed by the hydrogen adsorption on metal (Back *et al.,* 2006). Tsao *et al.* (2010) and Stuckert *et al.* (2010) claimed that Pt nanoparticles of ~1nm have remarkably increased the hydrogen storage capacity via spill over. Similar findings were also observed on the spill over effect of hydrogen adsorption on Pt/AC (Chen *et al.*, 2012; Wang *et al.*, 2014).

Tsao *et al*. (2010) reported hydrogen uptake of 0.3 to 0.6 wt.% by the spillover of Pt metal. This finding proved that the increasing of adsorption percentage might have strong correlation with the increasing in surface area. Fierro *et al.* (2010) also proved that hydrogen storage capacity is directly correlated with total surface area. They reported that the maximum excess of hydrogen capacity at 6.0 wt.% at -196 °C and 580 psig has been reduced to 0.6 wt.% at 25 °C and 725 psig. Their BET-N_2 values showed to be lower than 2630 $m^2.g^{-1}$. The uptake at -196 °C showed a correlation with micro-pore volume and strongly dependent on average pore diameter. In that study, activated carbons were treated with acid and doped with different platinum metal loading to enhance metal doped AC affinity to hydrogen, and thus increase the hydrogen adsorption. Hydrogen adsorptions at room temperature were studied with different range of pressure lower than the previous study, which are 150, 250 and 350 psig.

1.3 Objectives of Research

The objectives of this research are:

a. To synthesize and characterize the physical properties of activated carbon and platinum-doped activated carbon.
b. To evaluate the hydrogen adsorption capacity on various Pt loadings (0.5, 1, 2, 5, and 10 wt.%).

1.4 Scopes of Research

i. The synthesis process of platinum on commercial activated was carried out using wet-impregnation method. The activated carbon was treated with 2M HCl prior to impregnation with platinum. The 0.5, 1, 2, 5, and 10 wt.% of platinum loading on AC were prepared.
ii. The total surface area, surface morphology, surface metal content, metal phase crystallinity, metal reducibility and particle volumes of activated carbon, AC and Pt-doped activated carbon were characterized using BET-N_2, FESEM-EDX, XRD, TPR-H_2 and pycnometer, respectively.
iii. Hydrogen uptake for AC and Pt-doped AC were carried out using a volumetric method at room temperature with different pressure loadings of 150, 250, and 350 psig. The experimental rig of the equipment was built in-house based on Sievert type volumetric apparatus.

1.5 Significance of Research

Intensive effort on developing materials and systems for hydrogen storage to meet the world demand has gained attention of researchers. Application of hydrogen on transportation, stationary and portable power can be fulfilled with the presence of low cost and safe carbon-based storage materials. The findings of this study can offer the benefit of society considering that hydrogen plays an important role in future energy. The findings could lead to a better hydrogen storage and allow inexpensive carbon materials to store the gas at room temperature and low pressure. This study demonstrates hydrogen adsorption uptake on activated carbon incorporating platinum metal to bond hydrogen directly onto the Pt/AC surface. Bonding the hydrogen onto a highly porous material such as activated carbon makes it possible to have lighter, cheaper and safer hydrogen storage tanks.

1.6 Organization of Thesis

This thesis consists of five chapters and covers on the study of hydrogen adsorption on the activated carbon-doped platinum. Chapter 1 presents the background, including problem statements, objectives, and scopes of the study. Review on literature related to hydrogen energy, storage and its adsorption are presented in Chapter 2. The methodology covers on the preparation of adsorbents, wet impregnation of preparation, sample characterization, and hydrogen adsorption testing. The results and discussion are presented in the Chapter 4, which describes in detail the effect of different metal loadings and pressures in the adsorption. Summary of the findings and some practical recommendations to improve and upgrade the future works are included in Chapter 5.

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