CHAPTER 1

INTRODUCTION

1.1 Background and literature reviews

Since, Iijima discovered single-walled carbon nanotubes (SWCNTs) [1] and multi-walled carbon nanotubes (MWCNTs) [2], there were many studies of their properties such as molecular electronic, optic, nano-mechanic, magnetic and sensor properties [3-5]. Recently, there was growing interest in carbon nanotube material because of its specific chemical and physical properties such as chemical stabilities and high specific surface area [6]. There are two arrangements of carbon nanotubes: chiral and non-chiral (armchair and zigzag) structures depending upon their chiral vector (n and m) [7], as shown in Figure 1.1.

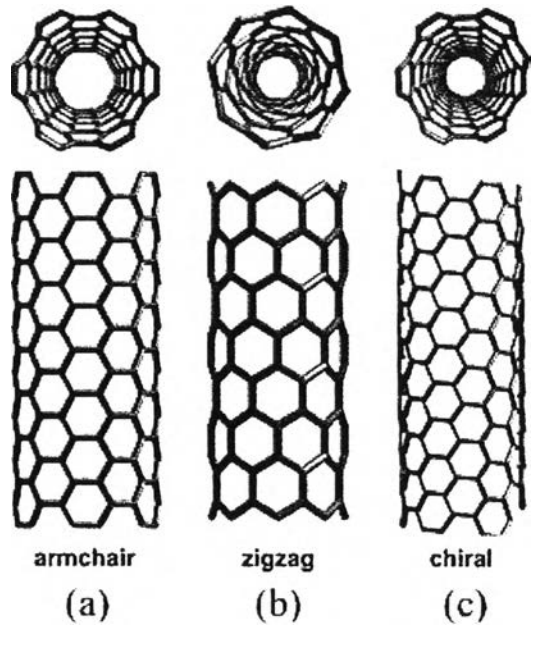

Figure 1.1 Molecular models of SWCNTs exhibiting different chiralities: (a) armchair (n,n), (b) zigzag (n,0) and (c) chiral (n,m) conformations. Top and bottom views inside and outside-wall of CNTs.

There were several investigations into the adsorption of small gases on SWCNTs such as H_2O, NH_3, NO_2, O_2, CH_4 and H_2 [8-11]. Adsorption of ammonia and nitrogen dioxide on carbon nanotube (CNT) [8, 9] were studied using density functional theory (DFT). The results showed that interaction of NH_3 and NO_2 molecules are physisorption; likewise, H_2 adsorbed on SWCNT [10]. The studies of various gas molecules (NO_2, O_2, NH_3, N_2, CO_2, CH_4, H_2O, H_2, Ar) adsorbed on SWCNTs and bundles [11]. It was found that most molecules adsorb weakly on SWNCTs. There was attempted to increase efficiency of gas adsorption on CNTs both experimental and theoretical studies by doping with metal atom [12, 13]. Gas adsorption on metal-doped CNT is obviously stronger than on the undoped SWCNT. Adsorption of H_2, CH_4, CO, and H_2S gases on site-selective electroplating of Pd, Pt, Rh, and Au metals on isolated SWCNTs were fabricated [12]. NO_2, H_2S and NH_3 adsorbed on Pt-, Pd–nanoclusters decorated on MWCNTs [13], and CO, NH_3, CO_2, CH_4 and CO sensor on Pt-doped SWCNT were investigated [14]. Adsorption of CO, N_2, O_2, NH_3 on Pt-doped (5,5) SWCNTs has been studied [15-17].

Hydrogen is the renewable energy source and a candidate for an alternative energy source [18]. Materials for hydrogen storage have been eagerly searched and synthesized due to their utility for renewable sources of energy. Adsorptions of hydrogen gas on the Pt atom at the sidewall of the (5,5) SWCNT as chemisorption resulting in the decomposition of H_2, and at the hemispheric caps as physisorption were found [19]. Adsorption energies (E_{ads}) of hydrogen molecule (H_2) adsorbed to Pt of the Pt–decorated (8,0) SWCNT of E_{ads} = 1.1 eV was found [20].

The hydrogen storage on Pt dispersion on MWCNT was studied and dissociation of hydrogen molecule to hydrogen atoms which form chemical bonding with the CNTs with higher energy of adsorption was found [21]. As many studies on the development of hydrogen gas sensors, Pt–doped SnO_2 nanowires [22], Pt–doped bead–like tin oxide nanowires [23] and Pt–doped on activated carbons/metal–organic frameworks–5 hybrid composites (Pt–ACs–MOF–5) [24] were investigated and enhancement in the H_2 response were found. The hydrogen adsorption and binding mechanism on metals, Ca, Sc, Ti and V decorated (8,0)SWCNTs were investigated using first principle calculations and their H_2 adsorptions with moderate adsorption

energies were found [25]. Increment of hydrogen storage capacity of CNTs decorated with alkali and alkaline earth metals such as Li, K [26, 27]. The results showed that alkali-doped CNTs can still adsorb nearly 2 wt% hydrogen [26]. In addition, Li-doped pillared single-wall nanotubes can lead to a hydrogen-storage capacity of 6.0 mass% [27]. CNTs supported transition metals such as Ti, V, Ni and Pd for their hydrogen storage were widely studied [28-31]. A single Ti atom coated on a SWCNT binds up to four hydrogen molecules and show that a SWCNT can strongly adsorb up to 8 wt% hydrogen [28]. The storage capacity of Pd- and V-doped CNTs were found to be 0.66 and 0.69 wt%, which are nearly 30% more than that of the pristine-CNTs [29]. Oxidation treatment to produce defects and subsequent loading with a Pd–Ni catalyst significantly increased the hydrogen storage capacity up to 6.6 wt% [30]. Highly dispersed Pd nanoparticles increases the H_2 adsorption on carbon surfaces [31].

Hydrogen adsorption isotherm for Pt–decorated (8,0)SWCNT at temperature range of 77–400 K was studied using molecular dynamics simulation and it was found that hydrogen adsorption on the Pt–decorated (8,0)SWCNT is significantly higher than the bare tube [32]. Theoretical studies on adsorption of hydrogen onto CNTs showed that low interaction energies between hydrogen and surfaces were found [11, 33-36]. Hydrogen storage on the Pt–decorated single–wall carbon nanohorns (Pt–SWCNHs) investigated using inelastic neutron scattering (INS) and Sievert's method measurements, it was found that hydrogen storage on Pt/SWCNHs with assistant of metal is activated at temperatures higher than 150 K [37].

Due to electronic properties of SWCNTs depending on their curvature, chirality and metal–decoration, these different characteristics should result different ability of their hydrogen adsorption. Therefore, study of hydrogen adsorption on novel metal such a platinum decorated on different curvatures of small lengths of closed–end SWCNTs should leads to obtain their appropriate characteristics for high potential of hydrogen adsorption. As it has been known that SWCNTs with diameters less than 0.4 nm [38-40] have outstanding electronic property specially metallic property, therefore SWCNTs of which diameters are small or smaller than diameter of (5,5)SWCNT are very interesting materials for hydrogen adsorption. Hydrogen

adsorption on novel metal decorated on different curvatures of cap of closed-end SWCNTs should also be explored to compare with side-wall.

1.2 Objective

In this work, hydrogen adsorption on platinum atom and Pt_n clusters (n=1 to 4) of Pt_n-decorated closed-end armchair (3,3), (4,4) and (5,5)SWCNTs has been, therefore, studied in order to obtain useful information of hydrogen adsorption and their corresponding adsorption sites. These adsorption information leads to extend research for syntheses and experimentally adsorption study of the relevant compounds. The most preferred adsorption sites for hydrogen on (3,3), (4,4) and (5,5)SWCNTs, adsorption reactions, their thermodynamic properties and rate constants have been explored and determined. The adsorptions of CO, O_2, N_2, CO_2, N_2O, NO_2, SO_2, H_2O and NH_3 on platinum atom of Pt_4-decorated (3,3), (4,4) and (5,5)SWCNTs were also obtained. Moreover, binding abilities of Rh_4, Ru_4, Os_4, Ir_4, Pd_4 on SWCNTs and hydrogen adsorptions on these surface have been studied.