CHAPTER 3

DETAIL OF CALCULATIONS

3.1 Computational method

Geometry optimizations of closed–end armchair (3,3), (4,4) and (5,5)SWCNTs, as shown in Figure 3.1. Their platinum group metals cluster (PGMs = Ru_4, or Rh_4, or Pd_4, or Os_4, or Ir_4, or Pt_n–cluster (n = 1 to 4)) decorated structures (PGM_n/SWCNTs) and their gas adsorption structures were carried out using DFT method. The (3,3), (4,4) and (5,5)SWCNTs are carbon clusters C_{48}, C_{68} and C_{110} of which carbon layers excluding caps are six, five and seven, respectively, see Figure 3.1. Three SWCNTs are composed of six layers and two hexagonal caps for closed–end armchair (3,3)SWCNT, five layers and two C_{14} caps for (4,4)SWCNT and seven layers and two C_{20} caps for (5,5)SWCNT. The hybrid density functional B3LYP, the Becke three–parameter hybrid functional [43] combined with the Lee–Yang–Parr correlation functional [53], using the LanL2DZ (Los Alamos National Laboratory 2–Double–Zeta) split–valence basis set [54-56] for platinum atoms, 6–31G(d) basis set [57, 58] for carbon atoms and 6–311++G(d,p) [59, 60] for hydrogen atoms have been employed in calculations. All calculations were performed with the Gaussian 03 program [61].

3.2 Definitions of reaction terms

3.2.1 Binding of PGMs cluster on SWCNTs

Geometry optimizations of closed–end armchair (3,3), (4,4) and (5,5)SWCNTs, their single platinum atom decorated structures (Pt/SWCNTs) were obtained. Naming system for binding single platinum atom onto (3,3), (4,4) and (5,5)SWCNTs is defined as Pt(N)/(n,n)SWCNT, where N is number of different C–C bond of which carbon atoms bind to platinum atom to form different adsorption configurations, otherwise not specified. Adsorption configurations of single platinum atom bound to carbon

atoms of the C–C bond numbers 1 and 2 of the (3,3)SWCNT are therefore named as Pt(1)/(3,3)SWCNT and Pt(2)/(3,3)SWCNT, respectively, as defined in Figure 3.1(a).
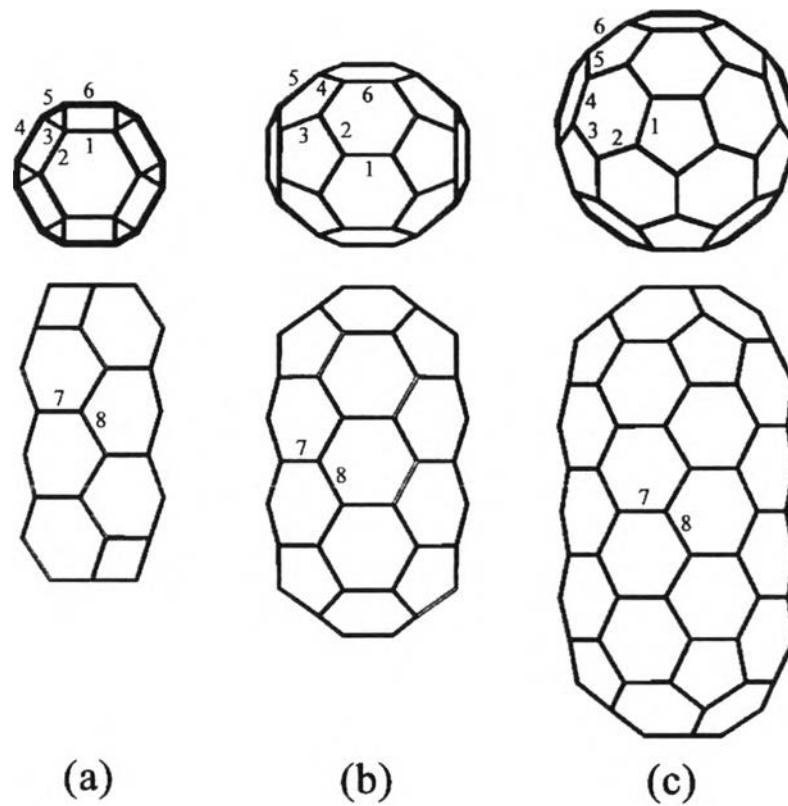
Figure 3.1 The B3LYP/6–31G(d)–optimized structures of closed–end (a) (3,3), (b) (4,4) and (c) (5,5) armchair SWCNTs and labeling of their C–C bonds which are binding positions of metal atom. Top and bottom are top and side views.

The structures of Pt_n (n=1 to 4), Rh_4, Ru_4, Os_4, Ir_4, Pd_4 cluster decorated on C–C bonds at closed–end cap were obtained. Binding energy ($\Delta E_{binding}$) of metal cluster adsorbed onto SWCNTs is defined by equation (3.1).

$$\Delta E^*_{binding} = E_{PGM_n-SWCNT} - \left(E_{SWCNT} + E_{PGM_n} \right)$$

(3.1)

Where $E_{PGM_n\text{-}SWCNT}$, E_{SWCNT} and E_{PGM_n} are total energies of PGM$_n$-decorated SWCNT, SWCNT and platinum group metals cluster, respectively.

3.2.2 Adsorption of small gases on PGM$_n$/SWCNTs

The adsorptions of H_2, CO, O_2, N_2, CO_2, N_2O, NO_2, SO_2, H_2O and NH_3 on platinum group metal group cluster of PGM$_n$-decorated (3,3), (4,4) and (5,5)SWCNTs were also obtained. Adsorption energy $\left(\Delta E_{ads}\right)$ of gas molecule on PGM$_n$-SWCNT is defined by equation (3.2).

$$\Delta E_{ads} = E_{gas/PGM_n/SWCNT} - \left(E_{PGM_n/SWCNT} + E_{gas}\right) \tag{3.2}$$

where $E_{gas/PGM_n/SWCNT}$, $E_{PGM_n/SWCNT}$ and E_{gas} are total energies of gas adsorption structure on PGM-decorated SWCNT, PGM-decorated SWCNT and gas molecule, respectively.

3.2.3 Thermodynamic quantities

The standard enthalpy ΔH_{298} and Gibbs free energy changes ΔG_{298} of adsorption of hydrogen molecule onto platinum of Pt$_4$ cluster decorated (3,3), (4,4) and (5,5)SWCNTs have been derived from the frequency calculations at the same level of theory. The equilibrium constant $\left(K\right)$ was computed using formula, $\exp\left(-\Delta G_{298}/RT\right)$.