

THE THERMODYNAMIC INVESTIGATION OF THE USAGE OF PYRENE AS A CARBON SUPPORT WITH PLATINUM CATALYST IN DIRECT METHANOL FUEL CELLS

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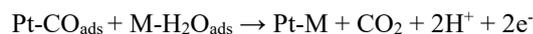
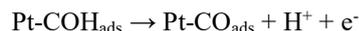
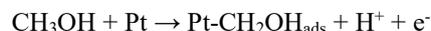
ABSTRACT

The anode of the direct methanol fuel cell (DMFC) includes methanol oxidation reaction which produces 6 moles of electrons per methanol molecule (the overall oxidation reaction: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$). This reaction is thought to occur in four steps with Pt catalyst producing Pt-CO_{ads} species at the last step which plays an important role in poisoning of the carbon support ($\text{CH}_3\text{OH} + \text{Pt} \rightarrow \text{Pt-CO}_{\text{ads}} + 4\text{H}^+ + 4\text{e}^-$). Generally, a second transition metal catalyst is used to overcome the surface poisoning problem. The second metal catalyst reacts with the main Pt catalyst to produce 2 more moles of electrons and converts CO_{ads} to free CO₂ ($\text{Pt-CO}_{\text{ads}} + \text{M-H}_2\text{O}_{\text{ads}} \rightarrow \text{Pt-M} + \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$). Therefore, the Pt-CO_{ads} species and the carbon support that holds it are the two key points. Pyrene, with its four fused benzene rings, was not used as a carbon support in the literature to the best of the knowledge. It has a D_{2h} symmetry point group which means that two of its benzene rings can act as binding surfaces for Pt-CO. (Note that CO is the reaction intermediate in CH₃OH oxidation.) Therefore, the present study included the calculation of the interaction Gibbs free energies ($\Delta G^{\circ}_{\text{int}}$) of the two possible complexes, Pyrene-PtCO Complex-1 and Pyrene-PtCO Complex-2 from their components of Pyrene-Pt_{ads} and CO. (In the reaction mechanism, first Pt is adsorbed on the carbon surface and then CH₃OH is bound to Pt. After that, CH₃OH is converted into CO by oxidation reaction.) DFT M06L/LANL2DZ theoretical level was used for the calculations. The results showed that $\Delta G^{\circ}_{\text{int}}$ of the two complexes had negative signs which denoted that both formations were spontaneous. $\Delta G^{\circ}_{\text{int}}$ of Complex-2 was -230.8 kJ/mole and was found to be about 25 kJ/mole more negative than that of Complex-1 (-206.1 kJ/mole). One of the reasons of this result might be explained like that: The calculated NICS(1) aromaticity value of the benzene ring to which Pt(CO)_{ads} was bound in Complex-2 was found to be higher compared to Complex-1. As a result, binding to the more aromatic ring produced the more stable complex. The other reason was thought to be the electrostatic charge distribution on the optimized pyrene ring which was obtained from the CHELPG analyses at the same level of theory. Complex-2 had a greater negative electrostatic charge on the benzene ring to which Pt(CO)_{ads} was bound compared to Complex-1. It was also concluded that the more stable complex, Complex-2, would need more energy for Pt-CO bond breakage and to combine with the second metal catalyst with respect to Complex-1 in a DMFC assembly.

Keywords: Pyrene, Carbon Support, Methanol Oxidation, DFT, M06L

Introduction

Direct methanol fuel cells (DMFC) convert the chemical energy of the methanol molecule to the electrical energy in their anodic half cells, directly. The overall oxidation reaction is known as $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$. The advantage of this reaction is that 1 mole of methanol molecule produces 6 moles of electrons. Mainly, platinum catalysts are used for this conversion on a carbon support (Samad et al., 2018) in which the possible reaction mechanism can be shown as below (Hamnett, 1997):



The Pt-CO_{ads} species produced at the 4th step plays an important role in a reaction mechanism hence it may stay as a surface poison on a carbon support if a proper second metal catalyst is not used in a proceeding reaction. Generally, the transition metal catalysts (mainly the Ru catalyst) are used to overcome the surface poisoning problem and convert the methanol completely to CO₂ (Park et al., 2014). Consequently, the surface poisoning (the Pt-CO_{ads} species) and the type of carbon support used are the two important points in this area.

Pyrene, with a chemical formula of C₁₆H₁₀, is a yellow solid and is the smallest peri-fused (where the rings are fused through more than one face) polycyclic aromatic hydrocarbon. It is generally produced by the incomplete

combustion of organic compounds. It has a planar molecular structure with D_{2h} symmetry point group. Figure 1 shows the chemical structure and ring numberings of pyrene molecule.

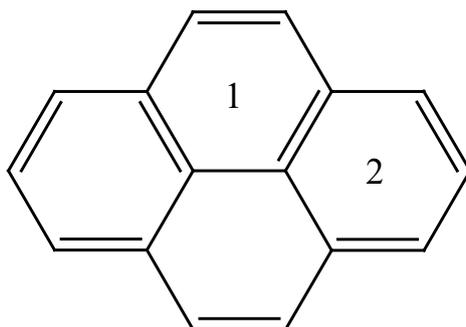


Figure 1. The molecular structure and ring numberings of pyrene molecule having D_{2h} point group.

It was not used as a carbon support in DMFC studies previously to the best of the knowledge. The D_{2h} symmetry in pyrene provides it to have two different kinds of benzene rings which means that two of these rings can bind to Pt-CO_{ads} species, separately. Therefore, the present study focused mainly on the calculation of interaction Gibbs free energies (ΔG°_{int}) of these two possible complexes.

Methods

All the calculations were performed in the gas phase using Gaussian 09 program software (Frisch et al., 2009). The structure optimizations were performed at DFT M06L/LANL2DZ level of theory. The interaction energies of both complexes were calculated using the same level of theory and corrected with basis set superposition error (BSSE) contributions (Ebrahimi et al., 2014). BSSE corrections use the Boys and Bernardi counterpoise technique (Ebrahimi et al., 2014) which are due to overlap of the wave functions of the moieties (Mottishaw and Sun, 2013). The calculations of the considered complexes contained zero point energy corrections and had no imaginary frequencies which indicated that they stood for no transition states or saddle points on the potential energy surfaces. The diamagnetic and paramagnetic effects of ring currents related to aromaticity and anti-aromaticity can be gauged by Nucleus Independent Chemical Shift (NICS) criterion (Schleyer et al., 1996). The NMR calculations were performed at the same level of theory using Gauge Independent Atomic Orbital (GIAO) method (Ebrahimi et al., 2014). Since NICS at 1 Å above the center of the ring, NICS(1), was recommended as a better aromaticity diagnostic than the NICS(0) (NICS at the center of the ring) (Ebrahimi et al., 2014), NICS(1) calculations were performed for the considered complexes.

The CHELPG (CHarges from ELectrostatic Potentials using a Grid based method) analyses were also performed at the same level of theory to evaluate the electrostatic charges distributed over pyrene molecule.

Results and Discussion

Structure Optimizations

The optimized structures of both the complexes titled as Pyrene-PtCO Complex-1 and Pyrene-PtCO Complex-2 were demonstrated in Figure 2. According to the structures, it was possible to mention that the platinum catalyst interacted with the edges of both Ring 1 and Ring 2 of pyrene, respectively (Figures 1 and 2). This statement was discussed in detail in the further section.

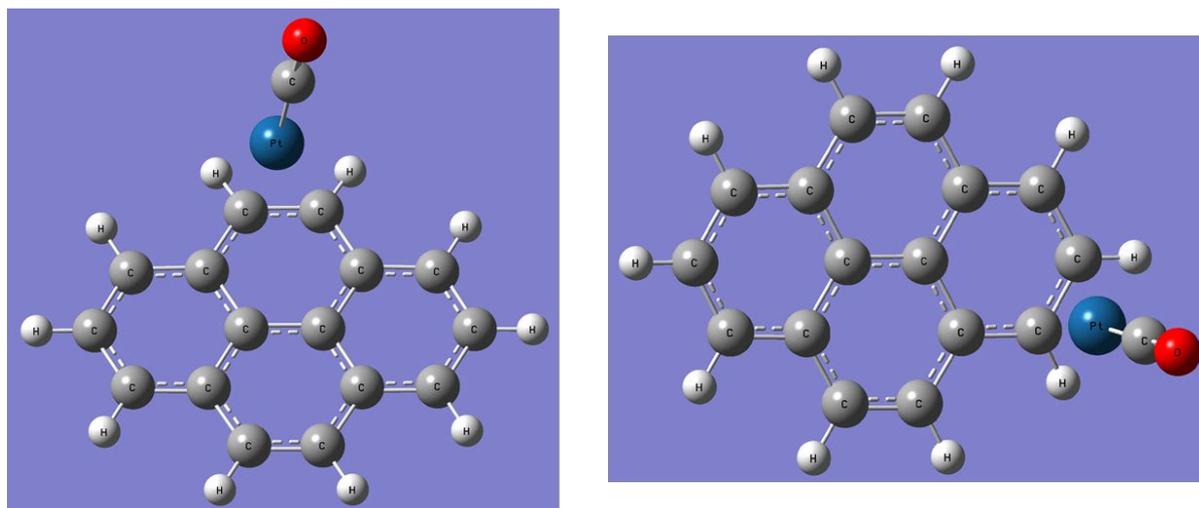


Figure 2. The optimized structures of Pyrene-PtCO Complex-1 (left) and Pyrene-PtCO Complex-2 (right) at the theoretical level of DFT M06L/LANL2DZ.

The Calculated Interaction Gibbs Free Energies of the Complexes

Before discussing this section, it is necessary to note that Pt is adsorbed on the carbon surface first and then CH₃OH binds to Pt. After that, CH₃OH is converted into CO by 4 steps oxidation reaction in the reaction mechanism which was presented previously. That was why Pyrene-Pt_{ads} and CO species were thought to be two different components of the interaction in the present study (Table 1). The interaction Gibbs free energies of the complexes were calculated according to the equation below in which ΔG°_{int} : standard interaction Gibbs free energy of the reaction, $G^{\circ}(\text{Complex})$: standard Gibbs free energy of the complex, $G^{\circ}(\text{Pyrene-Pt}_{ads})$: standard Gibbs free energy of the Pyrene-Pt_{ads} component, $G^{\circ}(\text{CO})$: standard Gibbs free energy of the CO component, BSSE: Basis Set Superposition Error.

$$\Delta G^{\circ}_{int} = G^{\circ}(\text{Complex}) - [G^{\circ}(\text{Pyrene-Pt}_{ads}) + G^{\circ}(\text{CO})] + \text{BSSE}$$

The values in Table 1 denoted that the formation of both complexes from their components were exothermic (spontaneous). However, the interaction Gibbs free energy of Pyrene-PtCO Complex-2 was found to be 24.7 kJ/mol more negative (more stable) than Pyrene-PtCO Complex-1.

Table 1. The calculated interaction Gibbs free energies of the complexes at the theoretical level of DFT M06L/LANL2DZ (1 au = 2625.5 kJ/mol).

	$G^{\circ}(\text{Complex})$ (au)	$G^{\circ}(\text{Pyrene-Pt}_{ads})$ (au)	$G^{\circ}(\text{CO})$ (au)	BSSE (au)	ΔG°_{int} (au)	ΔG°_{int} (kJ/mol)
Pyrene-PtCO Complex-1	-847.94730	-734.58217	-113.28072	0.00591	-0.07849	-206.1
Pyrene-PtCO Complex-2	-847.94476	-734.57029	-113.28072	0.00586	-0.08789	-230.8

The Calculated NICS(1) Aromaticity Values of the Rings of Pyrene

NICS(1) aromaticity analyses of Ring 1 and Ring 2 of pyrene were performed in order to explain the energy difference of interactions between the two complexes (Table 2). Both the considered rings of pyrene were aromatic but Ring 2 NICS(1) value was more negative than that of Ring 1. It indicated that Ring 2 was more aromatic than Ring 1 since the more negative NICS values implied the more aromaticity (Schleyer et al., 1996). This observation denoted that Pt and CO moieties bound stronger to Ring 2 compared to Ring 1 and as a result a more negative interaction energy was obtained in Pyrene-PtCO Complex-2.

Table 2. The calculated NICS(1) aromaticity values of the considered rings of pyrene at DFT M06L/LANL2DZ theoretical level.

NICS(1) (ppm)	
Ring 1	-6.53
Ring 2	-12.12

CHELPG Analyses of Pyrene Surface

CHELPG analyses of pyrene surface was performed at the same theoretical level and demonstrated in Figure 3. According to the charge distribution, the ESP charge of -0.279 located on two of the identical carbons of Ring 2. The two of the carbons of Ring 1 were also identical with the ESP charge of -0.216. (The complexes that bound to one of these identical carbons were investigated in the present study.) Consequently, the more negative charge located on Ring 2 made it possible to form a more stable complex, Pyrene-PtCO Complex-2.

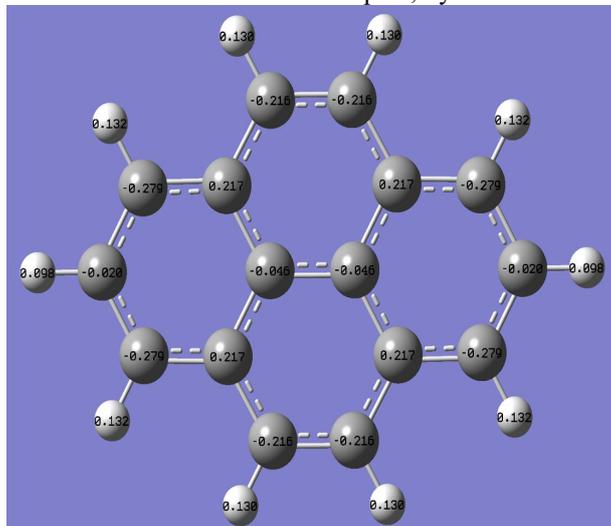


Figure 3. CHELPG analyses of the optimized pyrene at DFT M06L/LANL2DZ theoretical level.

Conclusion

The conclusion of this study were listed with two major outcomes:

1. Planar pyrene molecule might serve as a good surface for Pt catalyst in a direct methanol fuel cell since it had a potential of forming stable Pyrene-PtCO_{ads} complexes.
2. The more stable complex, Pyrene-PtCO Complex-2, would need more energy to break Pt-CO bond and combine with the second metal catalyst with respect to Pyrene-PtCO Complex-1 in a direct methanol fuel cell assembly.

Acknowledgements

The author would like to thank to Zonguldak Bulent Ecevit University Scientific Research Projects Coordination Office for financial supports (Projects No: BAP-2016-73338635-02 and BAP-2020-77654622-03).

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