

PtクラスターのH₂吸着，脱離に関する理論研究

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【Introduction】 The hydrogen is expected to substitute the fossil fuel and to be cost-effective, renewable, and clean alternative energy source. Fuel cells are used to gain energy from hydrogen. Catalysts are employed as electrodes in fuel cells. The properties of transition metals, particularly platinum possessing high resistance to chemical attack, high-temperature characteristics, and stable electrical properties makes it desirable in industrial applications as catalyst (platinum is important catalyst in hydrogenation). However its application in fuel cell implies additional restrictions regarding the amount of platinum required. The study of Pt-materials is important, providing understanding of hydrogen chemistry, and thus will contribute to development of cheaper, yet effective materials.

【Calculations Method】 Recently reported hydrogenated Pt-clusters were further studied here using RDFT method. Structures were reoptimized by Gaussian03 calculations employing the exchange-correlation functional PW91 with 6-31G** basis set for hydrogen atoms and LanL2DZ for Pt atoms. Energy density calculations were done with MRDFT program package using electron wavefunctions from Gaussian03 calculations.

【Result and Discussion】 The RDFT bond orders show redistribution of energy in a molecule and indicate bond strength in terms of energy density associated with stationary point of electron density between atoms. The bridge, tri-fold and four-fold bonding of hydrogen atoms have been explained in terms of bond orders and NBO analysis. The structure, energy density bond orders (b_e) and atoms identifiers of Pt₃H₁₂ cluster are shown in Fig.1. The RDFT bond orders indicate that the Pt⁽³⁾-H⁽¹¹⁾ bond strength is higher than Pt⁽²⁾-H⁽¹¹⁾ and Pt⁽³⁾-H⁽⁴⁾ bond strength is lower than Pt⁽²⁾-H⁽⁷⁾. Thus S_H→σ_{PtH}* interaction of bridging hydrogen is weak if the oppositeside Pt-H bond is strong. According to NBO analysis the bridging H atom is bonded via donor-acceptor interaction between hydrogen's (H⁽¹¹⁾) s-orbital and σ_{PtH}* antibonds (of terminal Pt⁽²⁾-H⁽⁷⁾ and Pt⁽³⁾-H⁽⁴⁾ bonds, with S_H→σ_{PtH}* 95.5 kcal/mol and 134.4 kcal/mol of NBO second-order perturbation theory stabilization respectively).

Fig.2 presents chemical potential (μ) mapped on interface surface of kinetic energy density around Pt₂H₁₀. The regions of higher chemical potential

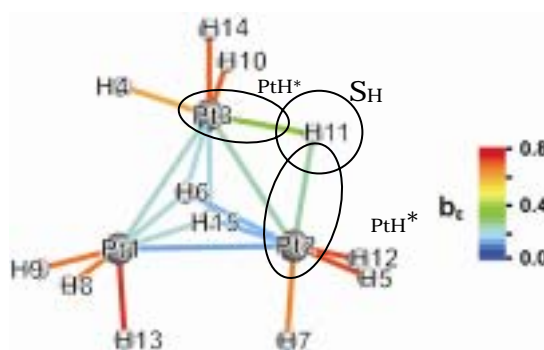


Fig.1 The energy density bond order (b_e) and atoms numbering in Pt₃H₁₂ cluster

around hydrogen atoms are associated with reduced electron density. However there also appear electron density deficient regions with lower chemical potential near surface exposed Pt atoms. These regions occur only in small clusters (up to five Pt atoms). The regions of lower electronic chemical potential on interface surface in proximity of Pt atoms coincide with non-spindle structure arisen tensile stress regions (Fig.3 black circle), as result of strong electric potential of poorly shielded Pt nucleus (marking strengthen acceptor properties of σ_{PtH}^* of trans Pt—H bond and lone pair donating property). The electronic chemical potential is the effective potential experienced by electrons. The low μ means poor shielding and strong electric potential of nucleus. Therefore regions of low electronic chemical potential are “electrophilic” centers. We had looked closer to these spots, of lower chemical potential, in $Pt_2H_{n=8,10,12}$ clusters (Fig.4) and found that these are reactive regions, able to stabilize H_2 molecule ligands via synergistic, σ -bond interactions. The H—H ligand bond lengths ($\sim 0.81 \text{ \AA}$) are found to be slightly elongated relative to “free” H_2 . Pt— H_2 distances are long ($\sim 1.92 \text{ \AA}$) relative to Pt—H terminal ($\sim 1.58 \text{ \AA}$) and bridging ($\sim 1.86 \text{ \AA}$) bonds, however are in typical range ($1.8 - 2.3 \text{ \AA}$) for σ -complex interactions. In addition each species from such interaction can stably exist independently (conformations of Pt_2H_8 fragment are almost same without or with adsorbed H_2) thus association and dissociation energy barriers are quite low. This somewhat resembles O_2 adsorbed on heme group. The HOMO-LUMO separation energies, listed in Table 1, show that from Pt_2H_8 to Pt_2H_{12} reactivity of the cluster is decreasing as H_2 occupies low μ sites.

We were able to visualize the reactive regions of Pt-clusters using electronic chemical potential calculated by RDFT method. Regions of low chemical potential were recognized as “electrophilic” centers characterized by electron withdrawing tensile stress. Through screen of chemical potential of other materials it is possible to quickly determine species able to reversible binding of H_2 .



Fig.2 Electronic chemical potential mapped on zero kinetic energy density isosurface of Pt_2H_{10} cluster

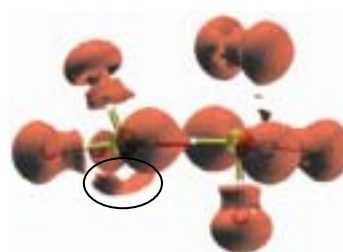


Fig.3 Stress tensor of Pt_2H_{10} cluster

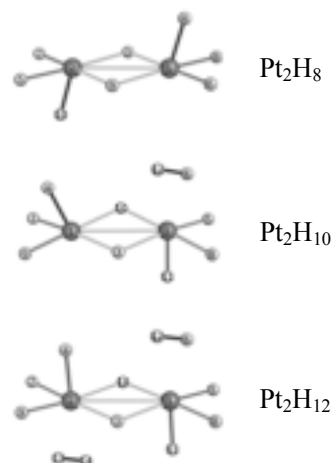


Fig.4 Models of Pt_2H_8 Pt_2H_{10} Pt_2H_{12}

Table.1 HOMO-LUMO orbital energies and energy gap of Pt_2H_8 Pt_2H_{10} Pt_2H_{12}

Cluster	E_{HOMO} [eV]	E_{LUMO} [eV]	$\Delta_{HOMO-LUMO}$ [eV]
Pt_2H_8	-7.2899	-4.1797	3.1103
Pt_2H_{10}	-7.2382	-3.5973	3.6382
Pt_2H_{12}	-7.1430	-3.0069	4.1361