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# Hydrogen storage capacity of Ti substitution-doped pyracylene: Density functional theory investigations

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## ABSTRACT

As candidates for hydrogen storage materials, Ti-doped pyracylenes, with a carbon atom replaced with a Ti atom, have been studied with density functional theory based method. Ti-doped pyracylene III with the Ti atom lying on a pentagon is the most stable isomer with substitutional energy of 4.73 eV/mol. Up to three H<sub>2</sub> molecules can be adsorbed on to the Ti atom through charge transfer and partially chemisorptions due to the partially filled d orbitals and positive charges on Ti. Totally seven H<sub>2</sub> molecules can be adsorbed on Ti-doped pyracylenes with mixture of chemo- and physisorption. Charge polarization induced electrostatic attraction is one of the major driving forces for physisorption.

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## 1. Introduction

Hydrogen gas has been recognized as the ideal replacement of petroleum fuels as it has high chemical energy, rich resource, and it is eco-friendly. However, the storage and transport of hydrogen gas hinder the mass applications of hydrogen energy. Studies on hydrogen storage will expedite its practical utilization. Vast majority of the efforts in hydrogen energy studies were devoted to the search for economically affordable material for hydrogen storage with high volumetric and gravimetric density, and high portability. Different types of hydrogen storage materials have been investigated experimentally and theoretically, e.g. novel high pressure-resistant containers [1], insulation materials for liquid hydrogen [2], materials physically adsorbing hydrogen [3–5], metals and complex hydrides for hydrogen's

intercalation [6], organometallic compounds partly chemically adsorbing hydrogen [7–9]. It is well known that transition metal atoms have partially occupied d orbitals. By ds (or dsp) hybridization, transition metal atoms can accept electrons to form complex with ligands by satisfying the 18-electron rule [10]. A single transition metal atom, which can adsorb up to six H<sub>2</sub> [11–13], might be good potential material for hydrogen storage. The formation of bulk materials of metal atoms upon release of hydrogen might lose the reversibility of the materials as hydrogen storage [8], thus transition metal cannot be directly used for hydrogen storage. The urgent problem to be solved is how to prevent transition metal atoms from forming bulk materials and to stabilize transition atoms with the d orbital available for hydrogen adsorption. Organometallic compounds with high stability would be such candidates. The strong C–C bonds produce

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stable frame in organic compounds. The strong stability of organic compounds and good affinity of transition metal towards hydrogen will be utilized in the present work to design ideal materials for hydrogen storage, e.g. TM–methylidynes with promising hydrogen storage capacity [7].

In the present work, Titanium doped pyracylene was designed for possible hydrogen storage. This designing is different from the idea of coordination of transition metal atoms with suitable Lewis-base (organic molecules with  $\pi$  bonds) [8,14]. Substitutional doping occurs in the Ti-doped pyracylene with strong Ti-C bonds. The repulsion between metal atoms due to the positive charge of Ti in the Ti-doped pyracylene could prevent aggregation of metal atoms upon release of hydrogen.

The structures of Ti-doped pyracylenes will be investigated within density functional theory (DFT) [15–17]. By means of nature bond orbital (NBO) [18] and molecular orbital (MO) analyses, the hydrogen adsorption of Ti-doped pyracylenes will be analyzed in detail.

## 2. Computational details

Four possible structures of Ti-doped pyracylene were designed according to the position a carbon atom was replaced. Generalized gradient approximation based DFT method mPWPW91 [19,20] with 6-31G(d,p) was employed to optimize the geometries of the systems. Through significant modification of the long-range behavior, mPWPW91 provides good description of noncovalent interactions [20]. The nature of the stationary points on potential energy surface was verified with vibrational frequency calculation. mPWPW91 with basis set 6-311++G(2df,2p) was used in single point calculations for properties analyses and better energy predictions.

All those calculations were carried out with Gaussian03 quantum chemical package [21]. The structures and MOs were plotted with GaussView [22].

## 3. Results and discussion

### 3.1. The geometries and electronic properties of Ti-doped pyracylenes

The Ti-doped pyracylenes have four different structures according to the position of substitution as shown in Fig. 1. The optimized structures of the Ti-doped pyracylenes were shown in Fig. 2.

Substitution energy ( $E_{\text{sub}}$ ) of C by Ti of Ti-doped pyracylenes was predicted (listed in Table 1) through  $E_{\text{sub}} = E(\text{C}_{13}\text{Ti-H}_8) + E(\text{C}) - E(\text{Py}) - E(\text{Ti})$ .  $E(\text{C}_{13}\text{Ti-H}_8)$  is the energy of the Ti-doped pyracylene,  $E(\text{C})$  is the energy of an isolated carbon atom in triplet,  $E(\text{Py})$  is the energy of pyracylene, and  $E(\text{Ti})$  is the energy of an isolated Ti atom in triplet.

All the substitutions are endothermic according to the substitution energies listed in Table 1. These substitutions can be realized through laser ablation. The substitution at position III costs the smallest amount of energies, while it costs the largest amount of energies at position IV among all

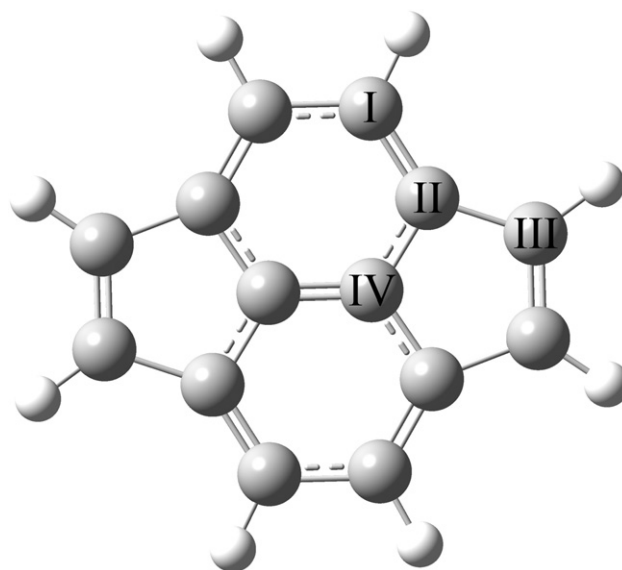


Fig. 1 – Structure of pyracylene and possible positions for substitution of Ti.

the structures investigated. Positions I and III have similar substitution energies with energy difference of 0.02 eV. Ti-doped pyracylene III is the most stable structure and I and III would be the major products during the production of Ti-doped pyracylenes.

The optimized structures of Ti-doped pyracylenes were plotted in Fig. 2. The Ti atom lies at the edge of pyracylene in Ti-doped pyracylene III and has the smallest destruction to the framework of pyracylene. The framework of pyracylene in Ti-doped pyracylene III has the smallest structural change with respect to the primitive pyracylene. This is the similar case for the substitution at position I. On the other hand, the structure of Ti-doped pyracylene IV has large destruction as the substitution occurs at the inner position of pyracylene, which destroys the  $\pi$  orbital conjugation of the carbon framework, thus costing the largest amount of energy for the substitution. Ti-doped pyracylene IV would be minor product of the substitution. Substitution at position II costs more energies than those at positions III and I while less than that at position IV.

As shown in Table 1, the Ti atom in the Ti-doped pyracylenes has large positive natural atomic (NA) charges and the repulsive interaction due to the positive charges prevents the aggregation of Ti-doped pyracylenes, thus ensuring the reversibility of hydrogen storage.

The doping of Ti brings about change of charges on its surrounding atoms. The NA charges of the surrounding atoms of Ti in Ti-doped pyracylenes were listed in Table 2. The most significant change of charge occurs on those hydrogen atoms connected to the Ti atom in Ti-doped pyracylenes I and III and they carry negative charges upon the doping of Ti. In those four different doping sites, the bonding of Ti with its surrounding atoms has different patterns. Only in the Ti-doped pyracylene III, Ti keeps the similar bonding pattern to that of the replaced carbon atom. In I, II, and IV, the bonding of Ti with its surrounding atoms varies with the substitution

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