

### **Abstract for Ph.D thesis**

**“A consideration on hydrogen storage properties of Pd/Pt nanoparticles by means of relativistic electronic-structure calculation”**

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Utilization of clean hydrogen energy has attracted public attention with the depletion of fossil fuels. For utilizing hydrogen energy, there are three essential techniques, *i.e.* hydrogen production, energy conversion and hydrogen storage. Especially, it has been considered to be the most important to establish hydrogen storage technique. Thus, many scientists and engineers have developed various hydrogen storage materials. Among them, hydrogen storage materials based on transition metals are superior to the other materials due to their hydrogen absorption/desorption abilities under a mild condition. As the amount of hydrogen storage is not enough for practical usage, however, further improvement of hydrogen storage materials has been still required. Conventionally, such a hydrogen storage material had been searched within a limitation of metal/alloy bulk. The limitation has caused several problems. First, degree of freedom for hydrogen absorption sites was limited by crystal structures of candidate materials. Then, since they are not molecular crystals, it is difficult to design novel crystal materials as we wish. Besides, not all combinations of metals can be alloyed in bulk scale. To overcome these problems, new class of hydrogen storage material is required now.

With the background, we focused on Pd and Pt nanoparticles synthesized by Yamauchi *et al.* in this study. The Pd/Pt nanoparticles were synthesized aiming to improve hydrogen absorption properties with the increase of the surface area. It has been well known that bulk Pd can absorb hydrogen, on the other hand, bulk Pt does not. They reported that Pt nanoparticle can absorb hydrogen as they expected. At the same time, however, they also reported that the amount of hydrogen absorption in Pd nanoparticle becomes smaller than that for bulk Pd [1]. Pd and Pt belong to the same group in the periodic table. Both bulk Pd and Pt have the face-centered cubic (fcc) structures with very similar lattice constants (Pd: 3.89, Pt: 3.92 Å). These facts indicated that the hydrogen absorption properties of Pd/Pt nanoparticles would be governed by their electronic structures rather than by their molecular structures. As Pd and Pt are heavy elements, it is not possible to neglect the relativistic effects to investigate electronic structures of their nanoparticles [2]. No systematic electronic structural investigation has been reported for Pd/Pt nanoparticles. There is no guiding principle to design nano-sized hydrogen storage materials using Pd/Pt.

The object of this thesis is to reveal the relationship between the electronic structure of Pd/Pt nanoparticles and their hydrogen storage properties. This thesis consists of five chapters. The outline of each chapter is as following.

In chapter 1, the development statuses of hydrogen energy and hydrogen storage materials were summarized. The purpose of this study was also described.

In chapter 2, the relationship between the electronic structure and hydrogen absorbing properties of Pd and Pt nanoparticles were discussed using relativistic quantum chemical calculations at the level of RI-PBE/def-SV(P). The amounts of absorbing hydrogen of Pd/Pt nanoparticles were observed to be 0.38 H/Pd and 0.15 H/Pt (Pd: 2.6±0.4nm, Pt: 3.2 nm). Our quantum chemical calculations applying  $M_{55}$  (M=Pd, Pt) cluster models showed that the hydrogen absorbing potential of Pd nanoparticle is more favorable than that of Pt nanoparticle (See Fig. 1). We also investigated an origin of the difference in the interaction between Pd/Pt nanoparticles and an H atom by localized molecular orbital energy decomposition analysis (LMO-EDA) [3]. The LMO-EDA showed that the instability of hydrogen in Pt nanoparticles originates from the exchange-repulsion interaction. Due to the relativistic effect, 5d valence electrons in a Pt nanoparticles have more diffuse spatial distribution than 4d valence electrons in Pd nanoparticles. This consideration could be also confirmed by ELF (electron localization function) analysis [4], which describes the distribution of closed electron pair in molecules (See Fig. 1). The natural charges of hydrogens in Pd<sub>55</sub> and Pt<sub>55</sub> were calculated to be -0.10 and +0.06, respectively. These results indicated that the electron distribution of the H atom in Pd nano particles is larger than that in Pt nano particles. Thus, it can be concluded that the lattice expansion of Pd nanoparticle was observed due to hydrogen absorption.

Our calculation results also well explain the reason why no lattice expansion of Pt nanoparticle upon hydrogen absorption was observed. This is because the size of a hydrogen atom becomes smaller in Pt nanoparticles. The hydrogen storage properties of Pd/Pt nanoparticles would be determined by the balance of electronic structure of the particles and the electronic state of absorbing hydrogen.

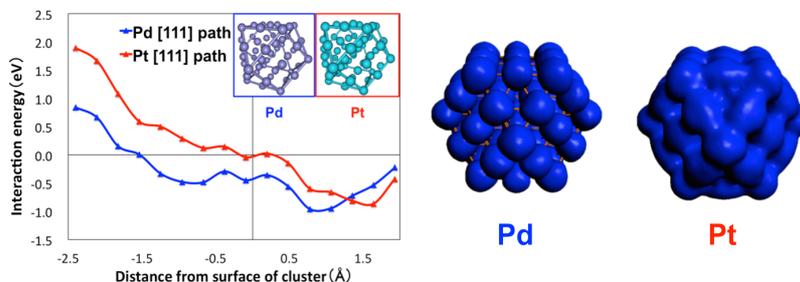


Fig. 1 (left) Hydrogen storage potentials (right) ELF of  $M_{55}$  ( $M=Pd, Pt$ )

In chapter 3, the relationships between the electronic structure and hydrogen absorbing properties of Pd/Pt alloy nano clusters (Fig. 2) were investigated using relativistic quantum chemical calculations at the level of RI-PBE/def-SV(P). The hydrogen absorption potentials are controlled by the structures (core-shell or solid-solution) and the chemical compositions of the alloy particles. A set of relativistic quantum chemical calculations showed that the Pd/Pt solid-solution nanoparticles with 10% Pt gives the best hydrogen storage ability. This follows experimental results well [5]. It was also found that the control of hydrogen storage ability can be explained by the diffuseness of ELF.

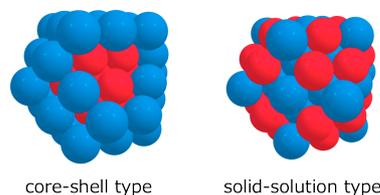


Fig. 2 Structure of Pd/Pt alloy nano cluster.

In chapter 4, the facet dependency of the hydrogen absorption rates for shape controlled Pd nano particles were investigated using reactive molecular dynamics (ReaxFF-MD [7]) simulations taking into account relativistic effects. It has been reported that the rate of hydrogen absorption reaction for the Pd nano-octahedron with {111} facets is 1.5 times faster than that for Pd nano-cube with {100} facets [6]. However, the rate tuning mechanism for the hydrogen absorption reaction has been unclear, since there has been no theoretical support on the experimental results. To clarify the mechanism, we investigated differences of hydrogen diffusion dynamics in Pd nano-octahedron and Pd nano-cube. The simulation results showed that the rate-determining steps of hydrogen absorption for the shape controlled Pd nano particles are hydrogen atom invasion process from the surface to the insides of the particles. It was also shown that the hydrogen diffusion coefficients in Pd nano-octahedron are larger than that in Pd nano-cube (See Fig.3). These results mean that controlling crystal facet is important for tuning hydrogen absorbing properties of nanosized hydrogen storage materials.

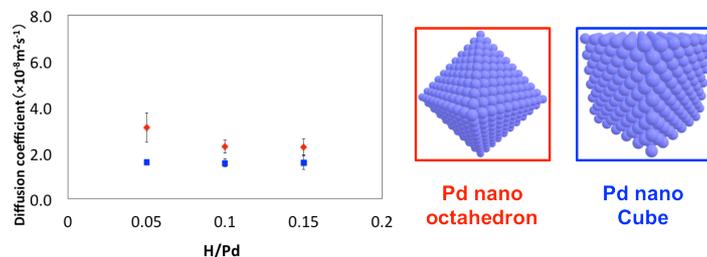


Fig. 3 The hydrogen diffusion coefficients for Pd nano-octahedron and Pd nano-cube

In chapter 5, this study was summarized.

**References** [1] M. Yamauchi *et al.*, *ChemPhysChem*, **10**, 2566 (2009). [2] H. Mori *et al.*, *Chem. Phys. Lett.*, **521**, 150 (2012) and references there in. [3] P. Su, H. *et al.*, *Chem. Phys.*, **131**, 014102 (2009). [4] A. D. Becke *et al.*, *J. Chem. Phys.*, **92**, 5397 (1990). [5] H. Kobayashi *et al.*, *J. Am. Chem. Soc.*, **132**, 5576 (2010). [6] G. Li *et al.*, *J. Am. Chem. Soc.*, **136**, 10222 (2014). [7] T. P. Senftle *et al.*, *J. Phys. Chem. C*, **118**, 4967 (2014).