

Electronic structures and hydrogen absorption properties of Pd/Pt clusters: What is the difference from bulk?

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[Introduction] Bulk Pd is a well-known hydrogen storage material. On the other hand, bulk Pt, which belongs to the same group 10, does not store hydrogen inside but only adsorb them on the surface. Recently, Yamauchi *et al.* investigated hydrogen storage ability of Pd/Pt nano cluster from pressure-composition (PC) isotherm. They expected the enhancement of the hydrogen storage ability by enlarging surface area of the material. The amount of hydrogen absorbed by the Pt nano cluster was enhanced as expected, however that by the Pd nano cluster was much smaller than that by the bulk Pd [1]. The experimental observations mean that the abilities for hydrogen absorption of the metal clusters are precisely controlled by the surface electronic structure of them. In this study, we investigated the differences of the hydrogen absorption properties between Pd and Pt clusters using electronic structure calculations.

[Methods] Resolution of identity DFT (RI-DFT) calculations with PBE exchange correlation functional and def-SV(P) basis sets were performed to investigate the electronic structure of the Pd/Pt clusters [2]. First, structures of the Pd₅₅ and Pt₅₅ were optimized with cubooctahedral (O_h) symmetry that was observed by X-ray diffraction experiments [1] (See Fig. 1). Then, the potential energy of H atom in/on the Pd/Pt clusters at grid points of a total number of 17×17×17 (a grid interval is 0.25 Å) were calculated to obtain hydrogen absorption potential energy surface. Natural population analysis was also performed at each grid point.

[Results] Fig. 2 shows that 2D views of potential energy surface (PES) cutting along the Y-Z plane of clusters (See Fig. 1). Figs.2 (a) and (b) show contour plot of the adiabatic potential energy surface for the hydrogen atom, at x = -0.25 and at x = -1.0, respectively. As shown in Fig. 2(a), we could observe much broader stable funnel for Pd₅₅ than for Pt₅₅. We also found that the octahedral site of Pd (Fig. 2(b)-left) is more stable than that of Pt. These results indicated that the hydrogen atom in the Pd₅₅ cluster can diffuse into the further inside more easily compared with Pt₅₅. The differences of enhancement of the hydrogen storage ability between Pd and Pt clusters will be further discussed in the poster session.

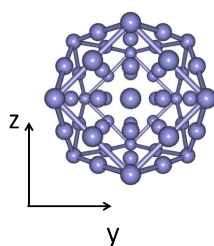


Fig.1 Optimized Pd₅₅ with cubooctahedral symmetry (O_h)

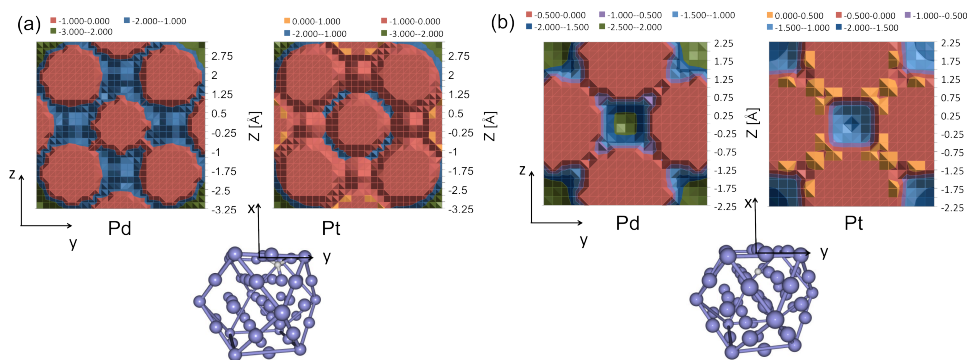


Fig.2 contour plot of the adiabatic potential energy surface for the hydrogen atom, at (a) x=-0.25 (b) x=-1.0

Reference [1] M. Yamauchi *et al.*, *Chem. Phys. Chem.*, **10**, 2566 (2009). [2] S. J. Grimme *et al.*, *J. Comput. Chem.*, **25**, 1463–1473 (2004).

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