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Importance of surface carbide formation on the activity and selectivity of Pd surfaces in the selective hydrogenation of acetylene

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ABSTRACT

A recent experimental investigation (*Kim et al. J. Catal. 306 (2013) 146–154*) on the selective hydrogenation of acetylene over Pd nanoparticles with different shapes concluded that Pd(100) showed higher activity and selectivity than Pd(111) for acetylene hydrogenation. However, our recent density functional calculations (*Yang et al. J. Catal. 305 (2013) 264–276*) observed that the clean Pd(111) surface should result in higher activity and ethylene selectivity compared with the clean Pd(100) surface for acetylene hydrogenation. In the current work, using density functional theory calculations, we find that Pd(100) in the carbide form gives rise to higher activity and selectivity than Pd(111) carbide. These results indicate that the catalyst surface is most likely in the carbide form under the experimental reaction conditions. Furthermore, the adsorption energies of hydrogen atoms as a function of the hydrogen coverage at the surface and subsurface sites over Pd(100) are compared with those over Pd(111), and it is found that the adsorption of hydrogen atoms is always less favoured on Pd(100) over the whole coverage range. This suggests that the Pd(100) hydride surface will be less stable than the Pd(111) hydride surface, which is also in accordance with the experimental results reported.

1. Introduction

Selective hydrogenation of acetylene is widely used to remove acetylene from ethylene feed in the industry [1,2]. The most commonly utilized catalysts for this process are based on Pd, such as PdAg [3–11], PdAu [12,13], PdZn [14] and PdGa [15–18]. The main issues in the selective hydrogenation of acetylene are the activity of the catalysts for the acetylene conversion, the selectivity of ethylene formation and the formation of higher molecular weight hydrocarbon species, known as green oil, which will lead to deactivation of the catalyst [1,2,19–23]. Our recent work systematically investigated the influence of surface structures, subsurface carbon/hydrogen, and surface alloying on the activity and selectivity in acetylene hydrogenation over Pd surfaces using density functional theory (DFT) calculations [24]. The formation mechanism of 1,3-butadiene, reported as the precursor of green oil production, was also thoroughly studied over Pd-based surfaces [25,26].

With the development of catalyst preparation methods, investigations on the influence of surface structures on the activity of catalysts can be rationally achieved experimentally. A good example of such a study was reported recently for the selective hydrogenation of acetylene [27]. Therein, monodispersed Pd nanoparticles with controlled shapes (cubes and spheres) were prepared to investigate the surface structure effect on the activity of the Pd catalyst for the selective hydrogenation of acetylene. The dominant surface termination of the cubic Pd nanoparticles was Pd(100) whilst Pd(111) dominates in spherical nanoparticles. The cubic Pd nanoparticles were found to exhibit higher acetylene conversion and ethylene selectivity than the spherical particles, leading to the conclusion that the Pd(100) surface should be more active and selective than Pd(111) towards acetylene hydrogenation.

In contrast, our recent DFT results concluded that the clean Pd(111) surface should have higher activity and selectivity for ethylene compared with the clean Pd(100) surface during acetylene hydrogenation [24]. Whilst this may indicate that the experimental and theoretical results are not consistent, it should be noted that one of the conclusions in our work was that the Pd catalyst might be carbide-like under the real hydrogenation conditions. We found that the activity of acetylene hydrogenation over clean Pd(111) was lower than over clean Pd(211), but this order was reversed when the activity over Pd(111) carbide and Pd(211) carbide surfaces were compared. It was also found that the order of the activity of the carbide surfaces is in accordance with the experimental results reported previously [28]. The carbide effect was only studied for the Pd(111) and Pd(211) surfaces in our previous work, since they are typical surface terminations to model the terrace and stepped sites of Pd surfaces.

In order to clarify the origin of the inconsistence between the experimental and theoretical results and identify the effect of carbide on the activity and selectivity order for the Pd(111) and Pd(100) surfaces

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compared with the clean surfaces, further studies on the formation of carbide phase over Pd(100) and the effect of carbide formation on the activity of acetylene hydrogenation have been undertaken and reported, herein. The hydride formation, which was reported in the experimental work, will also be discussed in this work.

2. Computational details

In the current work, DFT calculations were performed with the VASP simulation package in slab models [29–32]. The exchange–correlation functional PW91 with generalized gradient approximation (GGA) was employed to calculate the electronic structure [33]. The projector augmented wave (PAW) method was used to describe the interaction between the atomic cores and electrons [34,35]. For the calculations of Pd(111), Pd(100) and those surfaces with subsurface carbon/hydrogen atoms, four layer 2 × 2 unit cells were used to model the adsorption and reaction processes, and the top two layers were allowed to relax during optimization. A 5 × 5 × 1 *k*-point sampling in the surface Brillouin zone was used for the Pd(111), Pd(111)–carbide and Pd(111)–hydride surfaces while the *k*-point sampling used for Pd(100)-related surfaces was 3 × 3 × 1. It should be noted that, in these calculations, changes on the surface cell size on formation of the carbide were not considered as the coverage of carbon is relatively small and the surface structures obtained are consistent with those observed in previously reported experimental and theoretical studies. The vacuum height was set to be more than 12 Å. A cut-off energy of 500 eV and the force threshold on each relaxed atoms below 0.05 eV Å^{-1} were used in this work. The transition states were located with a constrained minimization method [36–38]. The adsorption energies are defined as:

$$E_{ad} = E_{total} - (E_g + E_{slab}) \quad (1)$$

where E_{total} is the energy of the system after adsorption, E_g is the energy of the gas phase molecule and E_{slab} is the energy of the slab.

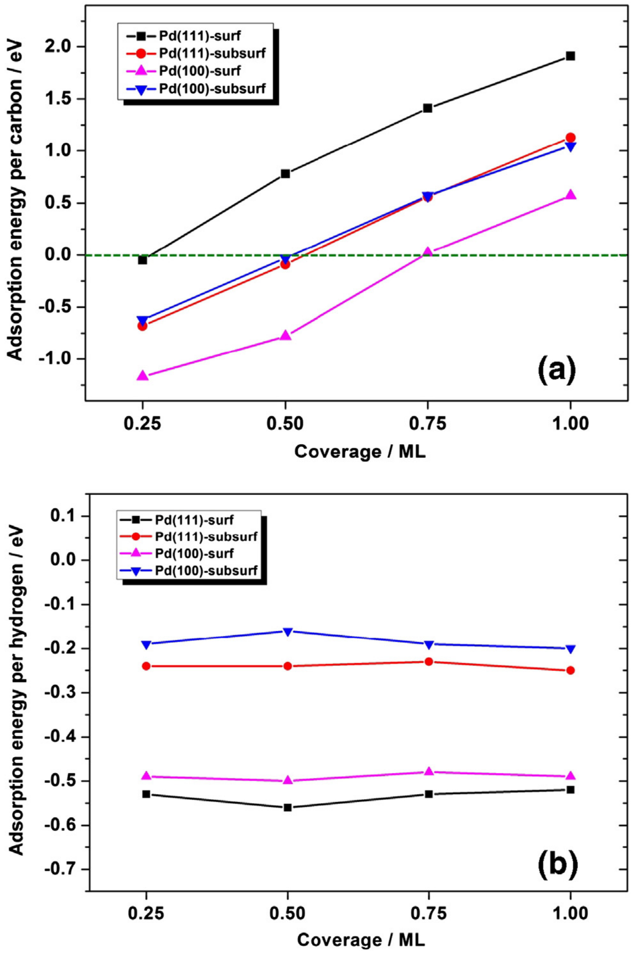

Fig. 1. (a) Trends of the adsorption energy per carbon atom at the surface and subsurface sites of Pd(100) as a function of the carbon coverage. The adsorption energy of carbon atom is calculated with respect to the energy of $^1/_2\,C_2H_2 - {}^1/_2\,H_2$, according to the equation of $^1/_2\,C_2H_2 \rightarrow C + {}^1/_2\,H_2$. (b) Trends of the adsorption energy per hydrogen atom at the surface and subsurface sites of Pd(100) as a function of the hydrogen coverage. The adsorption energy of hydrogen atom is calculated with respect to the energy of gaseous $^1/_2\,H_2$. Similar trends over Pd(111) surface are also included for comparison. Pd(111)-surf and Pd(111)-subsurf are the adsorption energies at the surface and subsurface sites of Pd(111), respectively. The same notation is used for Pd(100) and throughout this paper.

3. Results and discussion

The formation of surface and subsurface carbon over the clean Pd(111) and clean Pd(100) surfaces was examined first. The trend of the adsorption energy per carbon atom as a function of the carbon coverage at the surface and subsurface sites of Pd(100) was studied and compared with those obtained with previously reported data over the Pd(111) surface [24]. These data are shown in Fig. 1(a) and will be discussed later.

It should be mentioned that these carbon atoms are considered to be formed from the decomposition of acetylene over the catalyst surfaces. The energy profiles and the corresponding transition state structures of

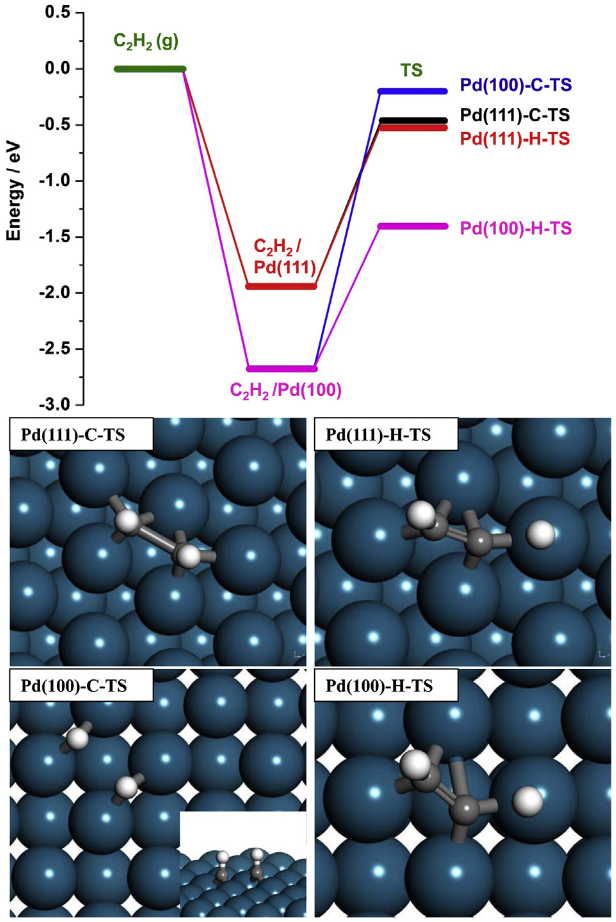

Fig. 2. Energy profiles of acetylene decomposition over clean Pd(111) and Pd(100) surfaces. The corresponding transition state structures are also shown here. Pd(111)–C–TS, Pd(111)–H–TS, Pd(100)–C–TS and Pd(100)–H–TS are the transition states of C—C and C—H bond scission over Pd(111) and Pd(100), respectively. The blue/underlying, grey and white balls are palladium, carbon and hydrogen atoms, respectively. This notation is used throughout this paper. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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