Journal of Catalysis 305 (2013) 264–276

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Influence of surface structures, subsurface carbon and hydrogen, and surface alloying on the activity and selectivity of acetylene hydrogenation on Pd surfaces: A density functional theory study ☆

Bo Yang [a], Robbie Burch [a], Christopher Hardacre [a,*], Gareth Headdock [b], P. Hu [a,*]

[a] CenTACat, School of Chemistry & Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, UK
[b] Johnson Matthey Catalysts, PO Box 1, Billingham, Teesside TS23 1LB, UK

ARTICLE INFO

Article history:
Received 1 February 2013
Revised 12 May 2013
Accepted 26 May 2013

Keywords:
DFT
Acetylene hydrogenation
Activity
Selectivity
Two-step model
Subsurface carbon and hydrogen
Surface alloy
Energy decomposition

ABSTRACT

The selective hydrogenation of acetylene to ethylene on several Pd surfaces (Pd(111), Pd(100), Pd(211), and Pd(211)-defect) and Pd surfaces with subsurface species (carbon and hydrogen) as well as a number of Pd-based alloys (Pd–M/Pd(111) and Pd–M/Pd(211) (M = Cu, Ag and Au)) are investigated using density functional theory calculations to understand both the acetylene hydrogenation activity and the selectivity of ethylene formation. All the hydrogenation barriers are calculated, and the reaction rates on these surfaces are obtained using a two-step model. Pd(211) is found to have the highest activity for acetylene hydrogenation while Pd(100) gives rise to the lowest activity. In addition, more open surfaces result in over-hydrogenation to form ethane, while the close-packed surface (Pd(111)) is the most selective. However, we also find that the presence of subsurface carbon and hydrogen significantly changes the reactivity and selectivity of acetylene toward hydrogenation on Pd surfaces. On forming surface alloys of Pd with Cu, Ag and Au, the selectivity for ethylene is also found to be changed. A new energy decomposition method is used to quantitatively analyze the factors in determining the changes in selectivity. These surface modifiers are found to block low coordination unselective sites, leading to a decreased ethane production.

1. Introduction

The selective hydrogenation of acetylene in excess ethylene is an industrially important process [1,2]. Ethylene is one of the most widely produced petrochemicals and is commonly made by the steam-mediated thermal cracking of higher hydrocarbons in high-temperature furnaces. However, the thermal processes also produce about 0.1–1% of acetylene and, importantly, acetylene poisons the downstream catalyst used for the polymerization of ethylene. Furthermore, the presence of acetylene also affects the quality of the poly-ethylene produced. The most widely used method to solve the problem is to selectively hydrogenate acetylene to ethylene using palladium-based heterogeneous catalysts. The objective is to hydrogenate acetylene to ethylene, leading to purification of ethylene and a higher ethylene yield.

The major concern in the acetylene removal processes consists of two issues, namely hydrogenation of ethylene to ethane and the formation of high molecular weight oligomeric species known as "green oil." The over-hydrogenation results in a loss of ethylene and reducing the effective reactant concentration for the subsequent polymerization, while green oil formation on the surface of the catalyst leads to the deactivation of the catalyst and also loss of hydrocarbon [3–5]. The challenge is to develop highly selective catalysts that have both low ethane production and green oil formation.

Extensive work has been undertaken, both experimentally and theoretically, to improve the performance of the widely used palladium catalyst by adding promoters such as metals, metal oxides, and modifiers such as CO [6] and N_2O [7,8]. Currently, the most commonly employed catalysts are based on supported Pd–Ag bimetallic systems [9–11]. Pd modified with Au [12], Cu [13], Ga [14–17], Pb [18], Zn [19], Ce [20], and K [21,22] have been used to improve the performance of the catalysts. Metal oxides such as CeO_2 [23], TiO_2 [24,25], Nb_2O_5 [26], and SiO_2 [27] have also been studied experimentally. In the search for non-precious metallic catalysts, Nørskov and co-workers used density functional theory (DFT) calculations to optimize the metal combinations and developed a highly selective Ni–Zn bimetallic catalyst that prevents over-hydrogenation [28]. More recently, Bridier and Pérez-Ramírez reported a ternary Cu–Ni–Fe catalyst with a relatively high

---

☆ This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

* Corresponding authors. Fax: +44 2890 974687 (C. Hardacre).

E-mail addresses: c.hardacre@qub.ac.uk (C. Hardacre), p.hu@qub.ac.uk (P. Hu).

0021-9517/$ - see front matter © 2013 The Authors. Published by Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcat.2013.05.027

selectivity to alkenes; however, in this case, significantly higher operating temperatures were needed compared with those used with the palladium-based systems [29]. Moreover, Ni–Al mixed oxides based on a hydrotalcite-type structure were also found to have a good selectivity for the hydrogenation of acetylene to ethylene [30]. In addition to promoters, the catalyst has been found to change during reaction with the formation of subsurface species like C and H. These are thought to have some effect on the selectivity of acetylene hydrogenation to ethylene [31–34].

Although acetylene hydrogenation reactions have been studied theoretically on both pure Pd and bimetallic Pd–Ag surfaces [35–40], the crucial role of the surface structures as well as the interplay between the surface structure and the presence of subsurface carbon and hydrogen species, since the formation of carbide or hydride during the hydrogenation may occur during the reaction of acetylene hydrogenation on Pd [31,32,41–44], and the effect of alloying on the activities and selectivity have yet to be described in detail. Therefore, in the current work, a number of surfaces have been studied, which are summarized below:

1. Flat (Pd(111) and Pd(100)) and stepped (Pd(211)) surfaces in order to examine the activity and selectivity for acetylene hydrogenation using DFT calculations. In addition, a defective Pd(211) surface containing lower coordinated Pd atoms than that on a standard Pd(211) surface has also been examined.
2. The effect of the presence of subsurface carbon and hydrogen species on the activity and selectivity of acetylene hydrogenation on Pd(111) and Pd(211).
3. The alloying effects of surface Cu, Ag, and Au on Pd(111) and Pd(211) and only the effects of them regarding the selectivity of ethylene formation are considered.

2. Computational details

DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP) in slab models [45–48]. The exchange-correlation functional PW91 was used to calculate the electronic structure with generalized gradient approximation (GGA) [49]. The projector augmented wave (PAW) method was employed to describe the interaction between the atomic cores and electrons [50,51]. For Pd(111), Pd(100) and those Pd(111) with subsurface species, surface alloys on Pd(111), four layer 2×2 unit cells with the top two layers relaxed during optimization were used to model the adsorption and reaction processes. Each surface alloy was modeled with the different coverage patterns was modeled with the substitution of surface Pd atoms with Cu, Ag, and Au atoms. A $5 \times 5 \times 1$ *k*-point sampling in the surface Brillouin zone was used for the Pd(111), Pd(111)–C, Pd(111)–H, and Pd–M/Pd(111) (M = Cu, Ag, and Au) surfaces while the *k*-point sampling used for Pd(100) was $3 \times 3 \times 1$. For Pd(211), defective Pd(211) and Pd(211) with subsurface species, surface alloys associated with Pd(211), 12 atomic layers with 1×2 surface supercells were employed with a $4 \times 2 \times 1$ *k*-point grid and the top 6 layers were relaxed together with the surface adsorbates. The defective Pd(211) surface, which is denoted as Pd(211)-defect, hereafter, was modeled by removing two Pd atoms at the step site thus forming two low-coordinated Pd atoms at the step site, as shown in the Supporting information. The surface alloys of Pd–M/Pd(211) (M = Cu, Ag, and Au) were modeled with the substitution of a whole row of Pd atoms at the step edge site with Cu, Ag, and Au. The vacuum was set to be more than 12 Å. A cutoff energy of 500 eV and the converging criteria of the force 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 [52–54]. The adsorption energies are defined as:

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

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.

López and co-workers recently studied the stability of Pd surfaces alloyed with Cu, Ag, and Au atoms [55]. They found that the solubility, near surface alloy formation, and islands formation of these metals on Pd surface were less favorable than other metals investigated. Therefore, in this paper, the Cu-, Ag-, and Au-doped Pd catalysts were modeled as surface alloys.

The free energies of gas-phase species were calculated using the equation $G = H - TS$. The entropic effect was only considered for the adsorption and desorption processes while the surface reaction energetics were estimated by the total energy ones. The temperature was set to 350 K, which lies in the range of the temperatures used under the industrial conditions (313–373 K). The total pressure was set to 10 atm and the partial pressures of C_2H_2, H_2, and C_2H_4 are 0.1 atm, 1 atm, and 8.9 atm, respectively, which are very similar to the experimental conditions. The entropies of C_2H_2, H_2, and C_2H_4 under standard conditions used in this paper were obtained from experimental databases [56,57]. The system studied herein is based on the front-end process wherein the H_2/C_2H_2 ratio is high and the selectivity to ethylene is the major problem. Therefore, the oligomerization of acetylene on the catalyst surface was not considered in the current work.

3. Results and discussion

3.1. Influence of surface structures on the activity and selectivity of ethylene formation on Pd

3.1.1. Ethylene formation from acetylene hydrogenation on flat and stepped surfaces of Pd

The adsorption energies for the reactant C_2H_2 and the product C_2H_4 and their adsorption geometries together with the adsorption geometries of the intermediate C_2H_3 on Pd(111), Pd(100), Pd(211), and Pd(211)-defect surfaces are shown in Table 1 and Fig. 1, respectively. On Pd(111), the adsorption geometries of these species are consistent with previous results, showing that the favorable adsorption of C_2H_2 and C_2H_3 occurs at the 3-fold hollow sites while C_2H_4 is bound in a di-σ configuration [34,35,58–66]. Similarly, hollow sites are preferred for the adsorption of both C_2H_2 and C_2H_3 on Pd(100). In this case, both C_2H_2 and C_2H_3 bind to four Pd atoms and the adsorption energy of C_2H_2 on Pd(100) is found to be much higher than that found on Pd(111). The adsorption geometry of C_2H_4 at Pd(100) is the same as that found on Pd(111), which shows a di-σ configuration. Again, the adsorption is stronger on the (100) surface compared with the (111) surface.

Comparing the step and corner sites, i.e., Pd(211) and Pd(211)-defect surfaces, respectively, shows that both the adsorption geometries and energies of C_2H_2 on each site are similar. The C_2H_2 was found to adsorb on the 4-fold site under the step edge (B5 site), whereas the C_2H_4 was found to adsorb on the step edge with a di-σ configuration, which is consistent with previously reported results [67]. The adsorption energy of C_2H_2 on Pd(211) is 0.1 eV lower than that on Pd(211)-defect site, but the adsorption energy of C_2H_4 on Pd(211) is only 0.01 eV higher than that on

Table 1
Adsorption energies (eV) of acetylene and ethylene on Pd(111), Pd(100), Pd(211), and Pd(211)-defect surfaces, which are calculated from Eq. (1).

	Pd(111)	Pd(100)	Pd(211)	Pd(211)-defect
C_2H_2	−1.94	−2.66	−2.26	−2.36
C_2H_4	−0.85	−0.96	−1.17	−1.16