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Density functional theory calculations of hydrogen dissociative adsorption on platinum-involved alloy surfaces

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ABSTRACT

Density functional theory calculations of the H_2 molecule over the Pt(111), Pt_4Pd_5(111), Pt_3Ir_6(111), and Pt_8Ru_1(111) surfaces were carried out to derive key properties involving interactions and electronic state of each atom. From the calculations, H_2 dissociative adsorption shows the lowest barrier in case of the Pt_3Ir_6(111) surface. Pt_4Pd_5(111) and Pt_8Ru_1(111) surfaces show a small energy barrier, while the Cu(111) surface is the highest energy barrier. The difference in the reactivity of H_2 molecule with the surface is pointed out by the differences in the valence electron configuration of approaching hydrogen which is also verified from the density of state curve. The electronic structure plots illustrate the substituted atoms can interact with molecular H_2 projected on the surface d-orbital.

1. Introduction

Platinum (Pt) is the most widely used catalyst, in particular, anodic material used in polymer electrolyte membrane fuel cells (PEMFCs), which converts the chemical energy of the hydrogen and oxygen directly to electric energy [1,2]. With the presence of a metal catalyst, the first step involves the adsorption of molecular hydrogen on the metal surface, and then either by the dissociation of hydrogen molecules into atoms or by the dissociation into the ion and atom on a surface. Then, a hydrogen atom is transferred as a charge transfer procedure which is known to efficiently on, especially, Pt electrocatalysts, and called "Tafel-Volmer" mechanisms. The dissociation of molecular hydrogen steps are significantly believed to the rate-determining steps.

However, the use of PEMFCs with pure Pt is limited due to a high development cost [3]. As a result, the surface catalytic compositions along with a variation of electronic structures have been notable studied to improve the catalytic activity and also to increase the lifespan of the PEMFCs [2]. Thus, the synthesis of the modified Pt alloy and/or of non-Pt catalysts could significantly help reducing a use of pure Pt catalysts and the membrane electrode assembly (MEA) cost. Many researchers have developed the performance of PEMFCs through a reduction of pure Pt via alloying with possible nonnoble and noble metals [3–8]. Alloyed catalysts can provide several benefits which could be both specific activity enhancements and improved contaminant tolerance. The electrochemical oxidation of 100 ppm H_2 and 2% CO mixture on PtRu gas-diffusion electrodes (GDE) was examined using in-situ electrochemical impedance spectroscopy (EIS). The results showed that the best CO-tolerant electrocatalysts appeared in the ratio of 1:1 of PtRu alloy, which is four times more active than pure Pt in H_2/CO anode gas [7,8]. Weng et al. [9] applied the scanning electrochemical microscopy (SECM) to identify potential bimetallic catalysts (Pt-M, M is Pd, Ir, Ru). SECM screening results illustrated that catalyst of Pt_4Pd_5(111), Pt_3Ir_6(111), and Pt_8Ru_1(111) were the optimum composition of the catalysts for hydrogen sensors. Therefore, it is important to reduce the use of Pt and characterize their behavior to understand the effect of the H_2 on alloyed catalysts.

Although the experimental studies have done to all mechanistic details of the reactions, a time scale too broad to collect and clarified of all possibility of reactions. Nowadays, the potential energy surface (PES) has been used to evaluate these behaviors for H_2 reaction processes on the surfaces using the density functional theory (DFT) in the computational calculation approaches. Nobuhara et al. [10] suggested that the energy barriers for H_2 adsorption were varied depend on the surfaces [10,11]. The energy barriers are either small or negligible on the H_2/Ni(111), H_2/Pd(111), and H_2/Ti(0001) surfaces, while H_2/Mg(0001) shows high energy barrier. Arboleda et al. [12] found that the parallel orientation was favored for H_2 adsorption and the very low energy barrier was found for the hollow-top-hollow configuration pattern. For metal alloy surfaces, the PtRu(111) surface shows stronger H_2 binding

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energy than Pt(111) as discussed by Liu et al. [13]. Adnene and Hazar [14] reported that the O_2 adsorption energies were increased due to the involving metal (M) of Pd, Pt, and Ni on the gold sub-layer surface, suggesting that the addition of a second metal should enhance the performance of the catalyst. The differences in the adsorption energies will refer to the potentiality of the surfaces.

Herein, we selected the (111) crystallographic plane of Pt-based metal alloy series to calculate the potential energy to get insight into the fundamental properties effecting the enhanced activity of Pt-M(111) surfaces. Present study focuses on the adsorption of molecular H_2 above the Pt(111), Pt_4Pd_5(111), Pt_3Ir_6(111), Pt_8Ru_1(111), and Cu(111) surfaces as an attempt to explore the possible H_2 dissociative adsorption process on each surface. Moreover, alterations in the electronic states of the entire valence band were analyzed.

2. Methodology

2.1. Computational method

All calculations were performed based on the density functional theory (DFT) methods of the CASTEP package [15] in Material Studio 5.5 program of Accelrys Inc. [16]. The exchange-correlation energy using the generalized gradient approximation (GGA) [17] within the Perdew-Burke-Ernzerhof (PBE) [18] functional was applied. Ultrasoft pseudopotentials combined with a plane wave basis set up to a cutoff of 380 eV were used in order to obtain accurate energy for all system. For Brillouin zone integration, 6 × 6 × 4 Monkhorst-Pack *k*-points were used. No significant change in energy was observed performing calculations with larger sets of k-points. Convergence of all calculated total energy are set to a value of order 1×10^{-6} eV/atom, 1×10^{-5} eV/atom, 0.03 eV/Å and 1×10^{-3} Å for the electronic self-consistent iteration (SCF tolerance), energy, maximum force and maximum displacement, respectively.

2.2. Surfaces and adsorption model

The low index (111) face was taken as the representative surface for this study using a supercell technique [19] as it exhibits one of the highest electrocatalytic sites [1]. All (111) surfaces were build using a 2-layers surface slab with a vacuum thickness of 10 Å along [111]-direction in order to avoid the interactions between periodic configurations on the axis perpendicular to the surface. There are 9-atoms in each atomic layer corresponding to a 3 × 3 unit cell. Here, the Pt(111), Pt-M(111) and Cu(111) surfaces were built. For Pt-M alloys surfaces, Pt(111) model is substituted with a transition metal M (M is Pd, Ir, and Ru) based on a Pt(111) structure with the atomic ratios of 4:5 Pt/Pd, 3:6 Pt/Ir, and 8:1 Pt/Ru, respectively. The highest distribution of M in Pt-M (111) including symmetrical surrounding was selected in this study. In this case, the Cu(111) metal was designed as a negative control model [10].

H_2 dissociative adsorption is a unique processes included in the hydrogen atoms adsorption [9]. In this case, the geometry of the H_2 (adsorbate) over each metal surface was illustrated in Fig. 1a. For H_2 adsorption, the reaction pathways and orientations of H_2 was defined as hollow-top-hollow (H-T-F) where the center-of-mass (CM) of H_2 molecule is over the top site keeping its molecule axis parallel to the surface, while the two H atoms are oriented towards the hcp and fcc hollow sites on the surface (Fig. 1b). The adsorption of H atom above a top site is very weak and unstable in contrast to its adsorption on fcc and hcp hollow sites [11], thus, the direction of the CM of H_2 was located on a top site. In this case, the selected H-T-F path sets of H_2 bond distance (r), and the H_2 CM perpendicular distance (Z) from the surface as a series of (r, Z) coordinates are: (0.75 Å, 3.0 Å), (0.85 Å, 2.0 Å), (0.95 Å, 1.75 Å), (1.25 Å, 1.5 Å), (2.05 Å, 1.25 Å), (2.75 Å, 1.15 Å), (3.25 Å, 0.9 Å), and (3.25 Å, 0.75 Å), respectively.

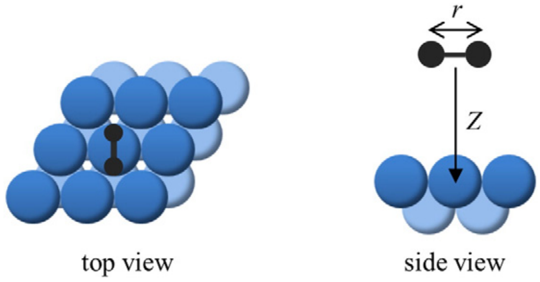

Fig. 1. Top view of H_2 orientation on the surfaces. The small circle indicates the hydrogen atoms, whereas the big circles represent the metal atoms in the first and second layers of the surfaces. The reaction pathways and orientations of H_2 are defined as hollow-top-hollow (H-T-F), it mean that the center of mass (CM) of H_2 molecule is over the top site while the two H atoms oriented in the hcp and fcc hollow sites on the surface.

The energy barrier of the H_2 molecular adsorbed on the surface was calculated in terms of the potential energy (E_{PE}) at each position point of the H_2 dissociative adsorption as a set of H—H bond length (r) and molecular H_2 height (Z) over the plane of the surface, which are defined as following equation;

$$E_{PE} = E_{adsorbate/slab} - [E_{adsorbate} + E_{slab}] \tag{1}$$

where $E_{adsorbate/slab}$ is the total energy of the surface slab with the H_2 on the surface, $E_{adsorbate}$ is the total energy of the isolated H_2 molecule, and E_{slab} is the total energy of the clear slab of the surface. According to this definition, negative E_{PE} value means exothermic adsorption, and a positive E_{PE} value means endothermic adsorption. Therefore, the negative values refer to the most favorable adsorption energy.

3. Results and discussions

3.1. Favorable H_2 adsorption

To determine the favorable optimum site and dissociative adsorption patterns of molecular H_2 on various Pt-M(111) surfaces, the geometry optimization calculations were performed. Results suggested that H_2 dissociative adsorption is probably difficult on Cu(111) surface. Table 1 presents the optimized energies by DFT calculation and atomic bond lengths for molecular H_2 on each metal surface. Fig. 2 shows the side view (left panel) and top view (left panel) of the optimized structure of H_2 on each surface. According to the optimization energy (E_{H_2}), the negative values refer to the most favorable adsorption energies. The results revealed that all the metal surfaces, except the Cu(111) surface, are tightly interacted with the H_2 molecule. The H_2 approaches the Pt(111) surface with E_{H_2} of −0.51 eV agree well with the previous DFT calculations (approx. −0.55 eV) [12].

Table 1 shows the optimization energy of H_2 molecule on various site of substrate atom of each surface. The H_2 molecule most likely

Table 1
Optimization energies (E_{H_2}) in eV and the H—H ($d_{H\text{-}H}$) and M-H ($d_{M\text{-}H}$) distance in Angstrom (1.0 Å = 0.1 nm).

	Pt (111)	**Pt_4Pd_5 (111)**		**Pt_3Ir_6 (111)**		**Pt_8Ru_1 (111)**		**Cu (111)**
		Pt	**Pd**	**Pt**	**Ir**	**Pt**	**Ru**	
E_{H_2}	−0.510	**−1.387**	−0.507	−0.926	**−1.013**	**−0.971**	−0.485	0.007
$d_{M\text{-}H}$	1.658	1.742	1.797	1.802	1.712	1.978	1.768	2.737
	(t)	(h)	(t)	(b)	(b)	(h)	(t)	
$d_{H\text{-}H}$	1.029	2.526	0.836	2.784	1.791	2.272	0.879	0.754

Note: Bold values refer to the most stable optimization energy in comparison with the pure Pt surface. (t), (h), and (b) refer to the adsorption over top, hollow and bridge site, respectively. The calculation was performed by $E_{H_2} = E_{adsorbate/slab} - [E_{adsorbate} + E_{slab}]$, where $E_{adsorbate/slab}$ is the total energy for the surface slab with the H_2 on the surface, $E_{adsorbate}$ is the total energy of isolated H_2, and, E_{slab} is the total energy of the bare metal surface, respectively.

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