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Density functional theory study of direct synthesis of H_2O_2 from H_2 and O_2 on Pd(111), Pd(100), and Pd(110) surfaces

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ABSTRACT

The direct synthesis of hydrogen peroxide (H_2O_2) from hydrogen (H_2) and oxygen (O_2) on Pd(111), Pd(100), and Pd(110) surfaces was investigated using periodic density functional theory (DFT) calculations. Several elementary steps making up this reaction were postulated and calculated. The Pd(111) surface shows the highest catalytic selectivity for H_2O_2 among the three surfaces. Open surfaces such as Pd(100) and Pd(110) are not favorable for this reaction because O–O-containing species on these surfaces dissociate easily. The O–O bond energy and the binding energy of O–O-containing surface species are responsible for catalytic selectivity. The higher binding energy of O–O-containing surface species is not favorable for the direct synthesis of H_2O_2 because the higher binding energy results in lower dissociation barriers.

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1. Introduction

Hydrogen peroxide (H_2O_2), a “green oxidant for the 21st century”, is an important chemical that is widely used in fields such as the textile industry, pulp/paper bleaching, waste treatment, and the fine chemical industry [1]. Since the reaction byproduct is water, H_2O_2 is regarded as the “greenest” environmentally friendly oxidant. The annual global demand for H_2O_2 is about 2 million tonnes.

Currently, H_2O_2 is produced industrially using a complex process involving the redox reactions of alkylanthraquinones and hydroquinone intermediates [2]. However, there are several drawbacks to the current process: the process is complex and unsafe, waste treatment is required, capital costs are high, and the byproducts are toxic. For environmental and economic reasons, the direct synthesis of H_2O_2 from H_2 and O_2 is an attractive alternative to the current anthraquinone autoxidation

process. Compared with anthraquinone autoxidation, direct synthesis has great advantages, e.g., anthraquinone, which is expensive, is not used, a one-step process is involved, and equipment investment costs are low.

The direct synthesis of H_2O_2 under ambient conditions has been studied for several decades. Pd-based (Pd or Pd alloy) catalysts have been found to be promising catalysts for the direct synthesis of H_2O_2 . Gosser et al. [3] obtained H_2O_2 concentrations of more than 35 wt% using Pd catalysts. Jones et al. [4] found that Au catalysts are favorable for this reaction in liquid media. Hutchings' group [5–20] investigated this reaction using Au and Pd-Au catalysts. Our studies have also demonstrated the promotional effects of Au and Pt on supported Pd catalysts, using a continuous reactor [21–23]. Currently, two problems associated with this reaction remain unsolved: (1) the wide explosive ranges of H_2 and O_2 , and (2) low selectivity as a result of formation of water as a byproduct. The

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key factors affecting H_2O_2 selectivity are the composition and structure of the catalyst, the promoter, and the liquid medium used in the reaction. The reaction mechanism has not yet been elucidated.

Density functional theory (DFT) calculations play an important role in understanding reaction mechanisms and structure–performance factors in heterogeneous catalysis. Some first principles calculations have been carried out for the direct synthesis of H_2O_2 [24–36], including slab models such as Pd(111), Pt(111), PdH(211), $\text{Au}_{0.89}\text{Pd}_{0.11}(221)$, Au/Pd(111), and PdAu/Pd(111), and cluster models such as Au–Ag, Au–Cu, Au–Pd, Au₁, Au₂, Au₃, Au₄, Au₅, Au₁₂, Au₁₃, Au₄₁Pd@Pd₁₃, AuPdM/Au(111), and Au₅₅. In the present paper, the reaction mechanisms for H_2O_2 synthesis on three different low-index surfaces, Pd(111), Pd(110), and Pd(100), were investigated using DFT calculations. Based on investigations of the reaction paths and the adsorption of surface species on these facets, we explored the effects of the surface structure of Pd, surface species, and elementary steps on the direct synthesis of H_2O_2 .

We assumed that the mechanism of the direct synthesis of H_2O_2 is a two-step hydrogenation, and that OOH is the important intermediate. Several elementary steps have been proposed for these reactions, as shown in eqs. 1–9:

where the asterisks (*) indicate surface species. Steps 1, 2, 3, 4, 5, and 9 are the six main elementary reactions for the formation of H_2O_2 from H_2 and O_2 . First, O_2 is hydrogenated to form an OOH intermediate species (step 4). Then the OOH species is hydrogenated to produce HOOH (step 5). In step 9, HOOH desorbs from the surface and H_2O_2 is eventually produced. The other elementary steps are side reactions and lead to water as a byproduct. Steps 6, 7, and 8 compete with steps 4, 5, and 9, respectively.

2. Methods

Binding energies and activation energies were computed using spin-polarized DFT calculations, and a plane-wave basis set with a cut-off energy of 400 eV was used to expand the Kohn–Sham wavefunctions. The interactions between the ionic cores and valence electrons were described using a projector-augmented wave method [37], and the exchange–correlation effects were self-consistently described within the Perdew–Burke–Ernzerhof generalized gradient approximation [38,39]. The Brillouin zone was sampled with a $(3 \times 3 \times 1)$ Monkhorst–Pack mesh of k points. The occupation of electronic states was determined using the Methfessel–Paxton method, and the smearing width was 0.2 eV. Optimized geometries were obtained using an energy convergence tolerance of

Fig. 1. Top views of Pd(111), Pd(100), and Pd(110) surfaces.

10^{-4} eV.

The three most common types of Pd surfaces, Pd(111), Pd(100), and Pd(110), shown in Fig. 1, were used to study the effect of the surface structure on H_2O_2 synthesis. A $1/6$ monolayer coverage was modeled using $p(2 \times 3)$ unit cell for Pd surfaces. Pd(111) was modeled as a three-layered slab, in which the topmost layer was relaxed, and the Pd(110) and (100) surfaces were modeled as six-layered slabs, in which the topmost two layers were allowed to relax, and the remaining layers were fixed at their bulk positions. An interslab spacing of 0.8 nm was found to be sufficient to avoid interactions between repeated slabs. The optimized lattice constant for the bulk Pd (0.389 nm) agrees well with the experimental value, 0.390 nm [40]. Binding energies were found to converge within 0.05 eV with respect to slab thickness, interslab spacing, and k -point sampling.

The binding energy (E_b) was calculated using the standard formula (eq. 10):

$$E_b = E_{\text{adsorbate/surface}} - E_{\text{clean}} - E_{\text{adsorbate}} \quad (10)$$

where $E_{\text{adsorbate/surface}}$, E_{clean} , and $E_{\text{adsorbate}}$ represent the total energies of the adsorbate–slab, the clean slab, and the adsorbate species in the gas phase, respectively. Different adsorption geometries of each adsorbate species were considered for all systems; only that with the lowest binding energy was reported.

The climbing image nudged elastic band (CI-NEB) method [41] was used to obtain an initial estimate of the transition-state structures. The NEB intermediate structure with the highest energy was taken as the initial estimate and further optimized to the transition-state structure. The transition states were verified using vibrational frequency calculations. The reaction energies (ΔE) of each elementary step were calculated as

$$\Delta E = E_{\text{FS}} - E_{\text{IS}} \quad (11)$$

where E_{FS} and E_{IS} are the total energies of the final state and initial state of the minimum-energy path (MEP), respectively. Negative values of E_b and ΔE indicate that the steps are exothermic and thermodynamically favorable. Conversely, positive values of E_b and ΔE indicate that the steps are endothermic and thermodynamically unfavorable. The activation energies (E_a) of the elementary steps were calculated as

$$E_a = E_{\text{TS}} - E_{\text{IS}} \quad (12)$$

where E_{TS} is the energy of the transition state of the MEP.

3. Results and discussion

3.1. Adsorption of reactants, intermediates, and products on Pd surfaces

Table 1

Binding energy (E_b), adsorption sites (site), and O–O bond lengths (d_{O-O}) of O_2 , H, O, OOH, OH, and HOOH species on Pd(111), Pd(100), and Pd(110) surfaces.

Intermediate species	Pd(111)			Pd(100)			Pd(110)		
	E_b /eV	d_{O-O} /nm	Site	E_b /eV	d_{O-O} /nm	Site	E_b /eV	d_{O-O} /nm	Site
O_2	–0.89	0.137	top-br	–1.69	0.143	br-br	–1.41	0.143	br(l)-br(l)
	–0.84	0.132	top-top				–1.37	0.143	br(s)-br(s)
							–1.39	0.133	top-top
H	–2.86	—	fcc	–2.81	—	hollow	–2.75	—	br(s)
				–2.78	—				
O	–4.64	—	fcc	–4.83	—	hollow	–4.31	—	br(s)
							–4.19	—	hollow
							–4.18	—	br(l)
OH	–2.60	—	br-titled	–3.02	—	br-titled	–3.06	—	br-titled
OOH	–1.21	0.147	top-top-br	–1.46	0.147	top-top-br	–1.58	0.148	top-top-br
HOOH	–0.26	0.147	top-top	–0.30	0.147	top-top	–0.40	0.148	top-top

br, br(s), and br(l) indicate bridge, short bridge, and long bridge, respectively.

In accordance with a two-step mechanism for hydrogenation in the target reaction, surface species such as H_2 , O_2 , H, O, OOH, OH, and HOOH were considered in our study. The adsorption of all these species on Pd(111), Pd(100), and Pd(110) surfaces were calculated. As shown in Fig. 1, there are top, bridge, and three-fold (face-centered cubic and hexagonal close packed) high-symmetry adsorption sites on the Pd(111) surface. For the Pd(110) surface, there are top, long bridge, short bridge, and four-fold adsorption sites. For the Pd(100) surface, three adsorption sites, i.e., top, bridge, and four-fold sites were considered.

The calculation results indicate that H_2 cannot adsorb on any of the three Pd surfaces in the molecular state, but dissociates into two H atoms during adsorption. There is no energy barrier in the dissociative adsorption of H_2 ; similar results have been reported by Yoshizawa [31]. The calculated binding energies, bond lengths, and site preferences of O_2 , H, O, OOH, OH, and HOOH on the Pd surfaces are listed in Table 1.

3.1.1 Adsorption of O_2 , OOH, and HOOH on Pd surfaces

O_2 , OOH, and HOOH are important intermediates in the direct synthesis of H_2O_2 . The adsorption configurations of these

Fig. 2. Adsorption configurations of O_2 , OOH, and HOOH species on Pd(111), Pd(100), and Pd(110) surfaces. Pd, O, and H are indicated by blue, red, and white balls, respectively.

three adsorbates are presented in Fig. 2.

The Pd(111) surface shows the lowest surface energy among the three Pd facets. There are two adsorption sites for O_2 on Pd(111), namely top-bridge and top-top. For the top-bridge sites, the O_2 molecules stretch from the top sites to the bridge sites; for top-top sites, two oxygen atoms connect near top sites. As seen from the data in Table 1, the binding energies of these two adsorption sites for O_2 are -0.89 eV and -0.84 eV, respectively, and the O–O bond lengths are 0.137 nm and 0.132 nm, respectively. The top-bridge site is 0.05 eV more stable than the top-top site. The surface O_2 species keep the same configuration as neutral O_2 molecules in the gas phase, but the bond length of the surface O_2 species (0.137 nm) is larger than that in the gas phase (0.124 nm). This indicates that the O–O bond of O_2 is weakened on binding to the Pd(111) surface.

The most stable site for O_2 on the Pd(100) surface is bridge-bridge, where both O atoms bind to bridge sites. The binding energy is -1.69 eV, and the O–O bond length is 0.143 nm. The O–O bond of O_2 on the Pd(100) surface is weaker than that on the Pd(111) surface.

The Pd(110) surface has the highest surface energy among the three Pd facets. The adsorption configurations of O_2 on the Pd(110) surface are more complicated compared with those on the other two facets. As shown in Fig. 2, the possible adsorption sites for O_2 on Pd(100) are bridge(long)-bridge(long), bridge(short)-bridge(short), and top-top. The binding energies of the corresponding configurations are -1.41 eV, -1.37 eV, and -1.39 eV, respectively, and the O–O bond lengths are 0.143 nm,

0.143 nm, and 0.133 nm, respectively. The O–O bond length of the top-top site (0.133 nm) is shorter than those for the other two configurations, but still longer than that in the gas phase (0.124 nm).

The configurations of OOH on the three Pd surfaces are quite similar. The two oxygen atoms in OOH bind to nearby top sites (Fig. 2), and the hydrogen atom in OOH points towards a bridge site, for all three surfaces. The OH bond in OOH tilts away from the surface for Pd(111), whereas it is roughly parallel to the Pd(100) surface. In the OOH configuration on the Pd(110) surface, two oxygen atoms are located between a top site and a four-fold hollow, and the OH bond in OOH tilts down to the surface. As listed in Table 1, the O–O bond lengths in OOH on the three adsorbed surfaces are almost the same, but are longer than those in O_2 species on these surfaces. This indicates that the O–O bond is weakened on formation of the O–H bond. The calculated binding energies of OOH on Pd(111), Pd(100), and Pd(110) are -1.21 eV, -1.46 eV, and -1.58 eV, respectively.

The configurations of HOOH on the three Pd surfaces are also rather similar, and our calculated results agree well with those reported in previous studies [29]. HOOH adsorbs on Pd surfaces through one hydrogen atom and one oxygen atom (Fig. 2). One OH bond in HOOH tilts down to the surface and the other OH bond slightly tilts away from the surface. In addition, the configurations of the surface HOOH species are nearly the same as those of H_2O_2 molecules in the gas phase. The binding energies of HOOH on Pd(111), Pd(100), and Pd(110) are -0.26 eV, -0.30 eV, and -0.40 eV, respectively.

Fig. 3. Adsorption configurations of H, O, and OH on Pd(111), Pd(100), and Pd(110) surfaces. Pd, O, and H are indicated by blue, red, and white balls, respectively.

3.1.2. Adsorption of H, O, and OH on Pd surfaces

The configurations of H, O, and OH are illustrated in Fig. 3. The dissociative adsorption of H_2 on Pd surfaces leads to two surface hydrogen species. The most stable site for hydrogen on the Pd(111) surface is a three-fold hollow site with a binding energy of -2.86 eV. For the Pd(100) surface, the binding energies of hydrogen for a four-fold hollow site and a bridge site are -2.78 eV and -2.81 eV, respectively. For the Pd(110) surface, hydrogen is adsorbed at bridge sites with a binding energy of -2.75 eV.

Similarly, the most stable adsorption site for oxygen on the Pd(111) surface is also a three-fold hollow site with a binding energy of -4.64 eV. For the Pd(100) surface, a four-fold hollow site is the preferred adsorption site for oxygen, with a binding energy of -4.83 eV. The calculated binding energies of oxygen on the Pd(110) surface are -4.31 eV, -4.18 eV, and -4.19 eV for long bridges, short bridges, and four-fold hollow sites, respectively.

As shown in Fig. 3, oxygen atoms bind to bridge sites, whereas hydrogen atoms point to hollow sites. For Pd(111), the O–H bond tilts away from the surface, whereas the O–H bond is almost parallel to the surface for Pd(100). For the Pd(110) surface, the oxygen atom is located between a bridge site and a four-fold hollow site, and the O–H bond tilts down to the surface. The binding energies of OH on Pd(111), Pd(100), and Pd(110) are -2.60 eV, -3.02 eV, and -3.06 eV, respectively.

3.2. Direct synthesis of H_2O_2 on Pd surfaces

Ideal catalysts enable easy dissociation of H_2 to H atoms, but are less active in the dissociation of O_2 . As we mentioned previously, H_2 directly dissociates into two H atoms, without any energy barrier, on the three Pd surfaces, and H atom adsorp-

Table 2

Activation barriers (E_a) and reaction energy (ΔE) of elementary steps in the synthesis of H_2O_2 on Pd(111), Pd(100), and Pd(110) surfaces.

#	Reaction	Pd(111)		Pd(100)		Pd(110)	
		E_a	ΔE	E_a	ΔE	E_a	ΔE
(4)	$O_2^* + H^* \rightarrow OOH^*$	0.58	-0.05	0.67	0.05	0.48	0.00
(6)	$O_2^* \rightarrow 2O^*$	0.78	-0.95	0.16	-0.12	0.24	-0.23
(5)	$OOH^* + H^* \rightarrow HOOH^*$	0.41	-0.26	0.44	-0.16	1.05	0.02
(7)	$OOH^* \rightarrow OH^* + O^*$	0.33	-1.56	0.26	-1.83	0.22	-1.46
(9)	$HOOH^* \rightarrow H_2O_2^*$		0.26		0.30		0.40
(8)	$HOOH^* \rightarrow 2OH^*$	0.30	-1.99	0.07	-2.37	0.10	-2.35

E_a and ΔE are given in eV. The numbering (#) corresponds to elementary steps that used in the introduction.

tion on Pd surfaces is very stable. The adsorption of O_2 on Pd surfaces is also stable. These two points suggest that Pd catalysts meet the basic requirements for the direct synthesis of H_2O_2 .

Our previous studies [21,22] have proved that Pd catalysts are highly active for H_2O_2 synthesis. The calculated reaction energies and activation energies of the elementary steps are listed in Table 2. The potential energy diagrams for this reaction are shown in Fig. 4.

We can see that the main reactions leading to the formation of OOH and HOOH species are those involving O–H bond formation, and the side reactions that cause the dissociation of O_2 , OOH, and HOOH species are those involving cleavage of O–O bonds. The selectivity with respect to H_2O_2 is therefore mainly determined by competition between O–H-bond-forming reactions and O–O bond cleavage reactions. A higher dissociation barrier for O–O bonds and a lower formation barrier for O–H bonds would therefore enhance H_2O_2 selectivity on Pd catalysts.

In our studies, the atomic densities of the surfaces decrease

Fig. 4. Potential energy surfaces for synthesis of H_2O_2 on Pd(111) (a), Pd(100) (b), and Pd(110) (c) surfaces. The main reactions and side reactions are indicated by green and red, respectively. The relative energy is given in eV.

in the order Pd(111), Pd(100), and Pd(110). As shown in Table 2 and Fig. 4, the order of the OOH dissociation barriers is Pd(111) > Pd(100) > Pd(110), and the order of the O₂ dissociation barriers is Pd(111) > Pd(110) > Pd(100). It is interesting to see from the data in Table 1 that the orders of the binding energies of OOH and O₂ are the opposite of those of the dissociation barriers on the three surfaces; that is, the higher binding energies for adsorbates containing O–O bonds lead to lower dissociation barriers. With regard to the atomic structure of the catalysts, the Pd–Pd bond length is longer than the O–O bond length of surface species. The higher binding energy of O–O species implies stronger interactions between Pd and O atoms. This strong interaction leads to easier O–O bond cleavage and lower selectivity for H₂O₂.

For the Pd(111) and Pd(110) surfaces, the dissociation barriers of adsorbates containing O–O bonds decrease in the order O₂, OOH, and HOOH with addition of H, indicating that the O–O bond is weakened by the formation of an O–H bond. The result is in good agreement with the investigations of Nørskov [24] on Au₁₂ clusters. The weakening of the O–O bond by addition of H partly contributes to the low selectivity of a pure Pd catalyst. The situation for the Pd(100) surface is similar to those for Pd(111) and Pd(110), but the dissociation barrier of O₂ is lower than that of OOH on this surface. According to our calculations, the lower dissociation of O–O bonds in O₂ than in OOH is consistent with a higher binding energy of O₂ than of OOH.

The dissociation barrier of HOOH on Pd(111) is the highest among those on the three Pd surfaces, and the dissociation barrier on Pd(100) is similar to that on Pd(110). In the adsorbed state of the final product, H₂O₂, two O atoms of HOOH can be partially charged by interacting with their adjacent H atoms, leading to a lower binding energy than those of OOH and O₂. Finally, H₂O₂ is produced by HOOH desorbing from the catalyst surface, with simultaneous dissociation of HOOH. As the HOOH binding energy increases, the desorption of HOOH becomes harder, and this is unfavorable for H₂O₂ production.

In summary, of the three surfaces studies, Pd(111) is the most favorable for the direct synthesis of H₂O₂ from H₂ and O₂, as illustrated by the following findings. (i) The dissociation barriers of O₂, OOH, and HOOH on the Pd(111) surface are higher than those on the other two surfaces. (ii) The formation barriers for OOH are almost the same on the three surfaces. (iii) The desorption energy of HOOH is lowest on Pd(111). In this study, the binding energies of O₂, OOH, and HOOH species on Pd(100) and Pd(110) surfaces, which have higher surface energies, are very high, and the higher binding energies weaken the O–O bonds of these adsorbates. Consequently, the weak binding of O–O in O₂, OOH, and HOOH enhances side reactions, thus the selectivity decreases for the direct synthesis of H₂O₂ on Pd(100) and Pd(110).

4. Conclusions

In this work, periodic DFT calculations were performed to study the direct synthesis of H₂O₂ on Pd(111), Pd(100), and Pd(110) surfaces. We first investigated the adsorption of H₂, O₂, H, O, OH, OOH, and HOOH on the three surfaces. Then the reac-

tion energies and activation energies of several elementary steps were calculated.

The selectivity for H₂O₂ formation is mainly determined by competition between O–H-bond-forming reactions and O–O bond cleavage reactions. The dissociation of O₂, OOH, and HOOH can lead to low selectivity. In addition, the O–O bonds of O₂ and OOH are weakened by adding H. Finally, the relationship between the dissociation barriers and binding energies for surface species containing O–O bonds were established.

The performance of a Pd catalyst is affected by the surface structure and the density of surface atoms. Among the three surfaces studied, Pd(111) shows the highest density of surface atoms and the lowest surface energy, hence the interactions between surface species containing O–O bonds and the Pd(111) surface are weaker than those for the other two surfaces, and Pd(111) exhibits the highest selectivity for H₂O₂ among the three surfaces.

We suggest that the dissociation of surface species containing O–O bonds could be suppressed, and the selectivity could be improved, by adding less active metals such as Au, Ag, and Cu to the Pd catalyst.

References

- [1] Campos-Martin J M, Blanco-Brieva G, Fierro J L G. *Angew Chem, Int Ed*, 2006, 45: 6962
- [2] Weissmehl K, Arpe H. *Industrial Organic Chemistry*. 3rd Ed. New York: VCH Publishers, Inc., 1997. 328
- [3] Gosser L W, Schwartz, J-A T. US Patent 4 772 458. 1988
- [4] Jones C A, Grey R A. US Patent 6 468 496. 2002
- [5] Landon P, Collier P J, Papworth A J, Kiely C J, Hutchings G J. *Chem Commun*, 2002: 2058
- [6] Edwards J K, Solsona B E, Landon P, Carley A F, Herzing A, Kiely C J, Hutchings G J. *J Catal*, 2005, 236: 69
- [7] Edwards J K, Solsona B E, Landon P, Carley A F, Herzing A, Watanabe M, Kiely C J, Hutchings G J. *J Mater Chem*, 2005, 15: 4595
- [8] Li G, Edwards J K, Carley A F, Hutchings G J. *Catal Today*, 2007, 122: 361
- [9] Edwards J K, Thomas A, Solsona B E, Landon P, Carley A F, Hutchings G J. *Catal Today*, 2007, 122: 397
- [10] Li G, Edwards J K, Carley A F, Hutchings G J. *Catal Commun*, 2007, 8: 247
- [11] Edwards J K, Hutchings G J. *Angew Chem, Int Ed*, 2008, 47: 9192
- [12] Ntainjua N E, Piccinini M, Pritchard J C, He Q, Edwards J K, Carley A F, Moulijn J A, Kiely C J, Hutchings G J. *ChemCatChem*, 2009, 1: 479
- [13] Solsona B E, Edwards J K, Landon P, Carley A F, Herzing A, Kiely C J, Hutchings G J. *Chem Mater*, 2006, 18: 2689
- [14] Edwards J K, Ntainjua N E, Carley A F, Herzing A A, Kiely C J, Hutchings G J. *Angew Chem, Int Ed*, 2009, 48: 8512
- [15] Edwards J K, Carley A F, Herzing A A, Kiely C J, Hutchings G J. *Faraday Discuss*, 2008, 138: 225
- [16] Pritchard J, Kesavan L, Piccinini M, He Q, Tiruvalam R, Dimitratos N, Lopez-Sanchez J A, Carley A F, Edwards J K, Kiely C J, Hutchings G J. *Langmuir*, 2010, 26: 16568
- [17] Pritchard J C, He Q, Ntainjua N E, Piccinini M, Edwards J K, Herzing A A, Carley A F, Moulijn J A, Kiely C J, Hutchings G J. *Green Chem*, 2010, 12: 915
- [18] Edwards J K, Thomas A, Carley A F, Herzing A A, Kiely C J, Hutchings G J. *Green Chem*, 2008, 10: 388

Graphical Abstract

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Density functional theory study of direct synthesis of H_2O_2 from H_2 and O_2 on Pd(111), Pd(100), and Pd(110) surfaces

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It is described that the direct synthesis of H_2O_2 from H_2 and O_2 on Pd(111), Pd(100), and Pd(110) surfaces using density functional theory calculations. Pd(111) exhibits the highest selectivity for H_2O_2 among the three surfaces.

- [19] Ntainjua N E, Edwards J K, Carley A F, Lopez-Sanchez J A, Moulijn J A, Herzing A A, Kiely C J, Hutchings G J. *Green Chem*, 2008, 10: 1162
- [20] Edwards J K, Solsona B, Ntainjua N E, Carley A F, Herzing A A, Kiely C J, Hutchings G J. *Science*, 2009, 323: 1037
- [21] Xu J, Ouyang L, Da G J, Song Q Q, Yang X J, Han Y-F. *J Catal*, 2012, 285: 74
- [22] Li P, He C H, Campestrini S, Corain B, Yuan W, Han Y-F. *Phys Chem Chem Phys*, 2010, 12: 2170
- [23] Xu J, White T, Li P, He C, Yu J, Yuan W, Han Y-F. *J Am Chem Soc*, 2010, 132: 10398
- [24] Grabow L C, Hvolbæk B, Falsig H, Nørskov J K. *Top Catal*, 2012, 55: 336
- [25] Todorovic R, Meyer R J. *Catal Today*, 2011, 160: 242
- [26] Li J, Staykov A, Ishihara T, Yoshizawa K. *J Phys Chem C*, 2011, 115: 7392
- [27] Li J, Ishihara T, Yoshizawa K. *J Phys Chem C*, 2011, 115: 25359
- [28] Ham H C, Hwang G S, Han J, Nam S W, Lim T H. *J Phys Chem C*, 2010, 114: 14922
- [29] Ford D C, Nilekar A U, Xu Y, Mavrikakis M. *Surf Sci*, 2010, 604: 1565
- [30] Ham H C, Hwang G S, Han J, Nam S W, Lim T H. *J Phys Chem C*, 2009, 113: 12943
- [31] Staykov A, Kamachi T, Ishihara T, Yoshizawa K. *J Phys Chem C*, 2008, 112: 19501
- [32] Wang F, Zhang D, Sun H, Ding Y. *J Phys Chem C*, 2007, 111: 11590
- [33] Joshi A M, Delgass W N, Thomson K T. *J Phys Chem C*, 2007, 111: 7384
- [34] Joshi A M, Delgass W N, Thomson K T. *J Phys Chem B*, 2005, 109: 22392
- [35] Wells D. *J Catal*, 2004, 225: 69
- [36] Rankin R B, Greeley J. *ACS Catal*, 2012, 2: 2664
- [37] Kresse G, Joubert D. *Phys Rev B*, 1999, 59: 1758
- [38] Perdew J P, Yue W. *Phys Rev B*, 1986, 33: 8800
- [39] Perdew J P, Burke K, Ernzerhof M. *Phys Rev Lett*, 1996, 77: 3865
- [40] Häglund J, Fernández Guillermet A, Grimvall G, Körling M. *Phys Rev B*, 1993, 48: 11685
- [41] Henkelman G, Uberuaga B P, Jonsson H. *J Chem Phys*, 2000, 113: 9901

Pd(111), Pd(100)及Pd(110)表面 H_2 和 O_2 直接合成 H_2O_2 的密度泛函理论研究

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摘要: 采用周期性密度泛函理论研究了 H_2 和 O_2 在Pd(111), Pd(100)及Pd(110)表面上直接合成 H_2O_2 的反应机理, 对反应的主要基元步骤进行了计算和分析. 结果表明, Pd(111)表面对 H_2O_2 直接合成的催化选择性最好, 表面原子密度较低的Pd(100)表面和Pd(110)表面上含有O—O键的表面物种解离严重, 不利于 H_2O_2 的生成. H_2O_2 的选择性与含有O—O键表面物种的O—O键能和表面物种的结合能有关. 含有O—O键的表面物种在表面的结合能越大, 越容易发生解离, 不利于形成 H_2O_2 .

关键词: 钯; 过氧化氢; 氢气; 氧气; 直接合成; 密度泛函理论

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1. 前言

作为“二十世纪绿色氧化剂”之一, H_2O_2 广泛用于纺织、造纸、污水处理和精细化工等领域^[1]; 它参与氧化反应后还原产物只有水, 不会产生其它副产物. 因此, H_2O_2 被认为是最“绿色”的环境友好型化学氧化剂. 其市场需求量随绿色经济增长而不断增加, 每年全球需求量大达200万吨以上, 我国已成为世界 H_2O_2 第二大消费国.

目前, H_2O_2 的工业生产方法主要是蒽醌法, 即通过对烷基蒽醌的连续加氢和氧化来合成 H_2O_2 ^[2]; 该法工艺复杂, 安全性低, 成本高, 还会产生大量有毒的副产物. 许多行业迫切需要在在线生产 H_2O_2 , 通过集成化反应以实现原子经济路线, 因此研发低廉的 H_2O_2 生产工艺有着十分重要的意义. 在催化剂作用下, H_2 和 O_2 直接合成 H_2O_2 (即 H_2O_2 直接催化合成法)是最有潜力取代蒽醌法的绿色合成方法, 它避免使用蒽醌中间体, 工艺简单及设备投资低, 是一种经济环保的反应路线.

研究发现, Pd基催化剂(纯Pd以及含Pd合金)是一种活性很高的 H_2O_2 直接合成催化剂. Gosser等^[3]用Pd催化剂在升温条件下得到了质量浓度大于35%的 H_2O_2 溶液. Jones等^[4]发现负载型Au基催化剂有利于液相 H_2 与 O_2 直接合成 H_2O_2 . Hutchings课题组^[5–20]对Au和双金属Pd-Au催化剂作了系统研究, 并取得了突破性进展. 本课题组深入研究了Pd, Pd-Au和Pd-Pt等合金催化剂的性能^[21–23], 发现Au和Pt对Pd催化 H_2O_2 直接合成的性能有显著的促进作用. H_2O_2 的直接催化合成主要面临两个问题: (1) H_2 和 O_2 混合物的爆炸极限很宽; (2) H_2O_2 直接合成过程中伴随副产物 H_2O 的生成, 且其生成在热力学上是有利的. 因此, 设计和制备高选择性催化剂是 H_2O_2 直接合成的研究重点.

密度泛函理论(DFT)在多相催化反应机理及催化剂构-效关系的研究中发挥着重要的作用. 人们对 H_2O_2 的直接催化合成进行了第一性原理模拟计算^[24–36], 其中包括表面平板模型Pd(111), Pt(111), PdH(211), $\text{Au}_{0.89}\text{Pd}_{0.11}$ (221), Au/Pd(111)和PdAu/Pd(111)等; 团簇模型Au-Ag, Au-Cu, Au-Pd, Au_1 , Au_2 , Au_3 , Au_4 , Au_5 , Au_{12} , Au_{13} , $\text{Au}_{41}\text{Pd}@ \text{Pd}_{13}$, AuPdM/Au(111)和 Au_{55} 等. 本文主要使用DFT研究 H_2O_2 合成在Pd(111), Pd(110)和Pd(100)三个低指数晶面上的反应中间物种和反应路径, 以探究Pd表面结构、表面物种和基元步骤对 H_2O_2 直接催化合成

反应机理的影响.

H_2O_2 在Pd催化剂上直接合成的反应机理为存在OOH中间物种的两步加氢还原过程, 包含的基元反应如下:

*表示表面吸附物种, H_2 和 O_2 反应生成 H_2O_2 必须经历(1)~(5)和(9)六个基元步骤, 其中反应(4)为第一步加氢反应, 生成OOH中间体; 反应(5)为第二步加氢反应, 生成HOOH; 最后经反应(9), H_2O_2 从催化剂表面脱附. 其它基元反应都不利于 H_2O_2 的形成并导致副产物 H_2O 的生成. 反应(6), (7)和(8)分别为(4), (5)和(9)的竞争反应.

2. 研究方法

本文使用周期性超胞方法进行DFT计算, 使用平面波基组来展开Kohn–Sham波函数, 平面波基组的截止动能(cut-off energy)设置为400 eV. 采用适合Pd过渡金属模拟的缀加投影波(PAW)方法来处理离子核与价电子之间的相互作用^[37], 并使用Perdew–Burke–Ernzerhof (PBE)泛函和广义梯度近似(GGA)交换关联势^[38,39]. 第一布里渊区的取样采用(3×3×1)的k空间Monkhorst-Pack网格, 并使用Methfessel–Paxton方法来决定电子占据状态, 展宽(smearing)设置为0.2 eV, 能量的收敛标准设置为 10^{-4} eV. 因为涉及含氧物质的吸附和反应, 在所有计算中都考虑自旋极化效应.

如图1所示, 使用周期性平板模型建立了Pd(111), Pd(100)和Pd(110)表面模型均由 $p(2\times 3)$ 的周期性平板构成, 吸附物种的表面覆盖率为1/6 ML. 其中Pd(111)表面模型包含三层平板, Pd(100)及Pd(110)表面模型含有六层平板. 平板模型在C轴方向设置0.8 nm的真空层, 以消除相邻平板间的相互作用. 对Pd(111)表面模型, 固定底部两层Pd原子的位置, 表层Pd原子和所有吸附物质原子可以在任意方向上发生弛豫; 对Pd(100)及Pd(110)表面

模型, 固定底部四层Pd原子的位置, 顶部两层Pd原子和所有吸附物种的原子可以在任意方向上发生弛豫. 通过计算优化, 得到体相Pd的晶格常数为0.389 nm, 和实验值(0.390 nm)^[40]基本一致. 经过测试, 发现增加平板层厚度、真空层厚度以及k点对吸附物种吸附能的影响十分微小(<0.05 eV), 现有的参数设置已经足够描述反应体系.

反应物、产物及中间体吸附物种在Pd表面的结合能(E_b)通过以下公式计算:

$$E_b = E_{\text{adsorbate/surface}} - E_{\text{clean}} - E_{\text{adsorbate}} \quad (10)$$

式中, $E_{\text{adsorbate/surface}}$, E_{clean} 和 $E_{\text{adsorbate}}$ 分别代表吸附态结构的总能量、清洁表面的能量以及吸附物种在气相中的能量. 计算中考虑了吸附物种的多种吸附构型, 但只报道了稳定吸附构型. 本文中所有能量相关物理量的单位为eV.

过渡态的搜寻采用 climbing image nudged elastic band(CI-NEB)方法^[41], 所有过渡态结构都通过频率计算验证. 各基元反应的反应能量(ΔE)通过以下公式计算:

$$\Delta E = E_{\text{FS}} - E_{\text{IS}} \quad (11)$$

E_{FS} , E_{IS} 分别表示最低能量路径(MEP)的终态(FS)和初态(IS)的能量. E_b 和 ΔE 为负值时表示相关过程为放热过程, 在热力学上是有利的; 为正值时则表示该过程是吸热过程, 在热力学上是不易进行的. 各基元反应的活化能(E_a)使用以下方程式计算:

$$E_a = E_{\text{TS}} - E_{\text{IS}} \quad (12)$$

E_{TS} 表示最低能量路径过渡态(TS)的能量. E_a 越小, 相关过程从动力学的角度来看更加容易进行; 反之, E_a 越大, 在动力学上是不利的, 相关过程越难发生.

3. 结果与讨论

3.1. 反应物、中间物种及反应产物在Pd表面的吸附

根据 H_2O_2 直接催化合成两步加氢机理, 反应涉及的物种包括: H_2 , O_2 , H , O , OOH , OH 和 HOOH . 本文首先研究了这些物种在Pd(111), Pd(100)和Pd(110)表面上的吸附情况. 如图1所示, Pd(111)表面包含top位、bridge位和3-fold hollow位(包括fcc和hcp位)三种吸附位置; Pd(110)表面包含top位、long bridge位、short bridge位和4-fold hollow位四种吸附位置; Pd(100)表面包含top位、bridge位和4-fold hollow位三种吸附位置.

结果显示, H_2 不能以分子形态在Pd(111), Pd(100)和Pd(110)表面上稳定吸附, 而是在吸附过程中直接解离为两个H原子, 而且没有解离能垒, 与Yoshizawa等^[31]的研究结果一致. 表1列出了 O_2 , H , O , OOH , OH 和 HOOH 吸

附物种在各表面的吸附能, 键长和吸附位置.

3.1.1. O_2 , OOH 和 HOOH 在Pd表面的吸附

O_2 , OOH 和 HOOH 是 H_2O_2 直接合成过程中至关重要的中间吸附物种, 图2描述了这三种物种在各表面的吸附构型.

Pd(111)是原子堆积密度最高的Pd晶面, 也是能量最低的; O_2 在其上主要有top-bridge及top-top吸附构型: 前者两个末端O原子分别吸附在top和bridge位, 后者两个O原子都吸附在Pd表面的top位. 如表1所示, 两种吸附构型的吸附能分别为-0.89 eV和-0.84 eV, O-O键长分别为0.137和0.132 nm. top-bridge吸附构型比top-top吸附构型更加稳定. 吸附态的 O_2 表面物种与气相中 O_2 构型区别不大, 但前者的O-O键长(0.137 nm)更长, 说明 O_2 在Pd(111)表面吸附后O-O键能减弱.

Pd(100)晶面的原子排布密度仅次于Pd(111)晶面, O_2 在其上最稳定的吸附位为bridge-bridge, 吸附能为-1.69 eV, O-O键长为0.143 nm; 与Pd(111)表面相比, 其表面 O_2 的O-O键能更小.

Pd(110)晶面是本文所研究的三个Pd晶面中原子排布密度最低的, O_2 在Pd(110)上的吸附构型比其它两个晶面更复杂. 如图2所示, O_2 在Pd(100)上有bridge(long)-bridge(long), bridge(short)-bridge(short)和top-top三种吸附构型, 吸附能分别为-1.41, -1.37和-1.39 eV, O-O键长分别为0.143, 0.143和0.133 nm. 三种吸附构型的稳定性差异较小, top-top吸附构型O-O键长(0.133 nm)小于其他两种吸附构型, 但仍然比 O_2 在气相中的(0.124 nm)大.

OOH 在三个表面上的吸附构型较为类似, 如图2所示, 两个O原子均吸附于top位, H原子指向bridge位; 而在Pd(111)表面, O-H键背离表面斜向上伸出. 在Pd(100)表面, O-H键几乎和表面平行, 有微小的斜向上趋势. Pd(110)表面上的 OOH 吸附构型与Pd(111)和Pd(100)表面上的 OOH 吸附构型相比, 差别较大, 两个top位O原子向4-fold hollow位有一定偏移, 且O-H键斜向下指向Pd表面. 如表1所示, OOH 在三个表面上的O-O键长接近, 但比 O_2 在三个Pd表面的O-O键长更长, 说明 OOH 吸附物种的O-O键能更弱, 即O-H键的形成减弱了O-O键能. OOH 在三个表面上的吸附能绝对值按Pd(111), Pd(100)和Pd(110)的顺序逐渐升高, 分别为-1.21, -1.46和-1.58 eV.

HOOH 在三个表面上的吸附构型也几乎一致, 我们计算的吸附构型与Ford等^[29]报道的基本吻合. 如图2所

示, HOOH通过一个H原子和一个O原子与Pd表面吸附, 一个O–H键与Pd表面接近垂直, 斜向下指向Pd表面, 另一个O–H键与Pd表面几乎平行, 斜向上背离Pd表面伸出, 这种吸附结构与气相中的 H_2O_2 结构基本相同. 与OOH的吸附类似, HOOH在Pd(111), Pd(100)和Pd(110)表面上的吸附能绝对值依次增大, 分别为–0.26, –0.30和–0.40 eV.

3.1.2. H, O和OH在Pd表面的吸附

H, O和OH在各表面的吸附构型如图3所示.

H_2 在Pd表面上吸附的过程中自动解离为两个H原子, 吸附H在Pd(111)上最稳定的吸附位为3-fold hollow位, 吸附能为–2.86 eV; 在Pd(100)表面, 吸附H的稳定吸附位主要包括4-fold hollow位和bridge位两种, 吸附能分别为–2.78和–2.81 eV; 在Pd(110)表面, 吸附H最稳定的吸附位为bridge位, 吸附能为–2.75 eV.

吸附O在Pd表面的吸附情况与吸附H类似. 在Pd(111)上最稳定的吸附位也是3-fold hollow位, 吸附能为–4.64 eV; 在Pd(100)上最稳定的吸附位为4-fold hollow位, 吸附能为–4.83 eV; 在Pd(110)上O的吸附位有long bridge位、short bridge位和4-fold hollow位三种, 吸附能分别为–4.31, –4.18和–4.19 eV.

OH在三个表面上的吸附构型基本一致, O原子吸附于bridge位, H原子指向hollow位. 不同的是, 在Pd(111)上, O–H键背离Pd表面向上倾斜; 在Pd(100)上, O–H键与Pd表面接近平行, 背离Pd表面略向上倾斜; 而在Pd(110)表面, bridge位上的O原子向hollow位有一定偏移, O–H键斜向下指向Pd表面, 这和OOH的吸附情况相似. OH在Pd(111), Pd(100)和Pd(110)表面上的结合能绝对值依次增大, 分别为–2.60, –3.02和–3.06 eV.

3.2. H_2O_2 在Pd表面的直接合成

本文提出负载型Pd催化剂表面 H_2O_2 直接合成的反应机理为 O_2 的两步加氢还原, 理想的 H_2O_2 直接合成催化剂首先应具备以下条件: H_2 和 O_2 容易在催化剂表面吸附, H_2 容易解离成H原子, O_2 不易在表面解离. 通过计算, 发现 H_2 在所研究的三个Pd表面都发生解离吸附, 没有解离能垒, H原子以较高的吸附能吸附在各Pd表面; O_2 在三个Pd表面也都能稳定吸附, 说明Pd金属催化剂基本符合 H_2O_2 直接合成的条件.

我们前期的实验结果证明, Pd是一种活性很高的 H_2O_2 直接合成催化剂^[21,22]. 通过DFT计算得到Pd(111), Pd(100)和Pd(110)表面上所有基元反应的反应能量和活化能列于表2. 图4为 H_2O_2 直接合成反应网络的势能面

(PES)图.

不难看出, 主反应 O_2 加氢生成OOH中间体及OOH加氢生成HOOH都是O–H键形成的反应, 而竞争副反应 O_2 , OOH和HOOH的解离都是O–O键断裂的反应, 因此决定 H_2O_2 选择性的主要是含有O–O键的表面物种O–O键断裂和O–H键形成反应的竞争. O–O键断裂越难, O–H键形成越容易, 则 H_2O_2 的选择性越高.

如表2和图4所示, 从Pd(111)表面到Pd(110)表面, OOH的解离能垒依次降低; O_2 的解离能垒则是在Pd(111)表面上最高, 在Pd(100)表面上最低. 由表1可知, OOH在三个表面上的结合能绝对值大小顺序为Pd(111) < Pd(100) < Pd(110); 而 O_2 在三个表面上的结合能绝对值由小到大依次为Pd(111) < Pd(110) < Pd(100). 推测表面含O–O物种的结合能越大, O–O键越容易断裂. 从催化剂原子结构上看, 催化剂表面的Pd–Pd原子距离远大于含O–O物种O–O原子间的距离, 结合能越大, Pd对O的作用越强, 从而导致O–O键能降低而容易发生断裂, 使得 H_2O_2 的选择性越低.

在Pd(111)表面, 含有O–O键的表面物种从 O_2 , OOH到HOOH, 随着H原子数逐渐增加, O–O的解离能垒逐渐降低, 即O–H键的形成削弱了O–O键的强度. 这和文献[24]在 Au_{12} 团簇上的研究结果一致: 含有O–O键的表面物种的O–O键能随含H原子数的增加而逐渐减小, 这是纯Pd催化剂上 H_2O_2 选择性不高的重要原因. O_2 , OOH到HOOH在Pd(100)和Pd(110)表面上的解离规律和在Pd(111)表面上的基本一致, 但是Pd(100)表面上 O_2 的解离能垒比OOH的低, 因为 O_2 在Pd(100)表面上的结合能比OOH的大, 削弱了O–O键, 因而 O_2 比OOH更容易解离.

HOOH的解离能垒在Pd(111)表面上最高, 而在Pd(100)和Pd(110)表面上相差不大. 与反应物 O_2 和中间体OOH不同, HOOH是最终产物 H_2O_2 的表面吸附态, 两个O原子可以分别从两个H原子获得部分电荷, 与Pd表面的作用减小, 因此HOOH的结合能比 O_2 和OOH的小. HOOH从催化剂表面脱附的竞争反应为HOOH解离成两个OH. HOOH在催化剂表面的结合能越大, 不仅使其脱附更困难, 其解离也更容易, 因而不利于 H_2O_2 的生成.

对比所研究的三个表面, 在Pd(111)表面上, O_2 , OOH和HOOH的解离能垒高于其它两个表面; OOH的生成能垒和在其它两个表面上相当; HOOH的生成能垒和脱附能垒均低于其它两个表面. 综合来看, Pd(111)表面最有利于 H_2O_2 的直接合成. Pd(100)和Pd(110)表面的表面原子密度比Pd(111)表面低, 表面能比Pd(111)表面

高,因而这两个面更加活泼,对含氧物种 O_2 , OOH 和 HOOH 的结合更加牢固,削弱了这些物种的 $\text{O}-\text{O}$ 键,有利于其解离生成 H_2O ,从而导致 H_2O_2 的选择性较差.因此,表面能较高的活泼表面不利于 H_2O_2 的直接合成.

4. 结论

采用周期性DFT计算方法研究了 H_2O_2 在 $\text{Pd}(111)$, $\text{Pd}(100)$ 和 $\text{Pd}(110)$ 表面上的直接合成,系统研究了 H_2 , O_2 , H , O , OH , OOH 和 HOOH 等物种在三个表面上的吸附,对基于 H_2O_2 直接催化合成两步加氢机理的9个表面基元反应的能垒和活化能进行了计算和分析.结果表明, H_2O_2 选择性主要取决于表面含 $\text{O}-\text{O}$ 物种中 $\text{O}-\text{O}$ 键断裂和 $\text{O}-\text{H}$ 键形成的竞争,其中, O_2 , OOH 和 HOOH 中 $\text{O}-\text{O}$ 键断裂的难易是影响 H_2O_2 选择性的主要因素. Pd 表面含

$\text{O}-\text{O}$ 物种中 $\text{O}-\text{O}$ 键的强弱是由该物种含 H 原子数和表面结合能共同决定的:含 $\text{O}-\text{O}$ 物种在 Pd 表面的结合能越大, $\text{O}-\text{O}$ 键越弱,越容易解离;含 $\text{O}-\text{O}$ 物种中 $\text{O}-\text{H}$ 的键形成削弱了 $\text{O}-\text{O}$ 键的强度.随着反应进行,含 $\text{O}-\text{O}$ 中间物种含 H 原子数逐渐增多, $\text{O}-\text{O}$ 键也越容易断裂,从而越容易发生解离副反应. Pd 催化剂上 H_2O_2 直接合成的性能主要是由催化剂表面的原子排布结构和密度决定的,其中 $\text{Pd}(111)$ 表面的表面原子密度最高,表面能最低,对 O 的结合作用较小,抑制了副反应的发生, H_2O_2 选择性高于较活泼的 $\text{Pd}(110)$ 和 $\text{Pd}(100)$ 表面.因此,通过向 Pd 催化剂中掺杂对氧结合较弱的 Au , Ag 和 Cu 等,使催化剂表面“钝化”,可抑制含 $\text{O}-\text{O}$ 键表面物种的解离,从而提高催化剂的选择性.该结果完善了 H_2O_2 直接合成机理的研究,为 Pd 基催化剂的设计和实验室制备提供了理论指导.