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Citation	Chemistry letters, 42(12), 1481-1483 https://doi.org/10.1246/cl.130710
Issue Date	2013-12-05
Doc URL	http://hdl.handle.net/2115/54745
Type	article (author version)
File Information	ChemLet_42_Draft4_3.pdf



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Density function theoretical investigation on the Ni₃PP structure and its hydrogen adsorption property of Ni₂P(0001) surface

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Electronic and structural properties of phosphorus terminated structure of Ni₂P(0001) surface (Ni₃PP) are investigated by density functional theoretical (DFT) calculation. Phosphorus adsorption largely stabilizes the Ni₂P(0001) surface by creating Ni-P bonds on the Ni trimer. Atomic hydrogen can adsorb on the topmost P site but its adsorption energy is much lower than its adsorption energy on the Ni trimer site of Ni₃P₂ surface. Our results suggest that the Ni trimer is the key factor for high catalytic activity.

Nickel phosphide (Ni₂P) shows a high catalytic activity for the hydrodesulfurization[1] and other hydrotreatment catalyses towards hydrodenitrogenation and hydrodeoxygenation and so on.[2] The key issue to understand the hydrogenation reactions is interaction between hydrogen with Ni₂P surface in an atomic level. The bulk structure of Ni₂P is composed of two different layers with different composition, Ni₃P₂ and Ni₃P₁, aligning alternately along the [0001] direction as shown in Figure 1(a). Rodriguez et al. showed that Ni₃P₂ surface was more stable surface than Ni₃P₁ surface and they discussed the hydrogen adsorption properties on the Ni₃P₂ surface.[3] However, scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) studies on the Ni₂P(0001) have revealed that the Ni₂P(0001) surface is mainly (about 80 %) covered with phosphorus on the Ni three fold site of Ni₃P₂ surface after 953 K annealing under UHV conditions with minor amount of uncovered Ni₃P₂ surface.[4-6] This new phosphorus covered surface is called as Ni₃PP surface. Similar phosphorus terminated surface was reported on the reconstructed (10-10) surface by STM observation[7]. The phosphorus termination of the surfaces were supported by

photoemission spectroscopy (PES) study.[8-10] Moreover, recent *in situ* XAFS studies show that the adsorption of sulfur on the Ni₂P creates the active phase.[11-13] Therefore the chemically modified Ni₂P surface is interesting not only the fundamental problem but also the catalysis applications. In the present study we have explored the density functional theoretical (DFT) work on the Ni₃PP surface to reveal the mechanism of P-covered surface formation and its hydrogen adsorption properties in comparison with the Ni₃P₂.

DFT calculations were performed using the Vienna ab-initio Simulation Package code (VASP 5.2.12).[14-16] The Perdew-Burke-Ernzerh exchange-correlation functional with a generalized gradient approximation [17,18] was used. Projector-augmented wave approach (PAW) [19,20] have been used together with plane wave basis sets. The optimized bulk Ni₂P lattice constants were $a = b = 0.5876$ nm, $c = 0.3365$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The Ni₂P(0001) surface was modeled with 12 atomic-layers periodic slab with a ca. 3.5 nm vacuum layer. The chemical formula of Ni₃P₂ and Ni₃PP are Ni₃₆P₁₈ and Ni₃₆P₁₉, respectively. The kinetic energy cutoff of 300 eV was used and the Brillouin zone was sampled by a $4 \times 4 \times 1$ Monkhorst-Pack [21] mesh. The z axis is taken as normal to the surface.

First, we compared the electronic structure of Ni₃PP and Ni₃P₂ surface to examine the stabilization mechanism of the surface. Figure 2(a) shows the density of states (DOS) of a Ni atom in the Ni trimer of the topmost Ni₃P₂ layer. Dotted and solid lines are DOS of Ni before and after the P coverage. The states appear in the energy range of -1 to -2 eV and a sharp peak around -0.5 eV of Ni on the phosphorus-uncovered Ni₃P₂ surface which are assigned to 3d states. The peak at -0.5 eV has a spread crossing the Fermi level. They are shifted downwards to the band between -1.5 and -4.5 eV and the peak at -3.9 eV by the interaction with phosphorus when the Ni₃PP structure is created. On the other hand DOS of P on the topmost Ni₃P₂ layer does not change so much. The DFT calculations suggest phosphorus adsorption largely stabilizes 3d states of surface Ni trimer which should be the driving force for the formation of Ni₃PP.

We calculated the hydrogen adsorption energy and electronic state of Ni₃PP surface. Table 1 summarizes the adsorption energies of atomic hydrogen on both surfaces, Ni₃PP and Ni₃P₂. Surface energies were calculated by following expression:

$$E_{ad} = E_{H+Ni_2P} - \left(\frac{1}{2} E_{H_2} + E_{Ni_2P} \right),$$

were E_{H+Ni_2P} , E_{H_2} and E_{Ni_2P} correspond to total energy of hydrogen adsorbed on Ni₂P, isolated hydrogen molecule and isolated surface, respectively. Both hydrogen and surface structures are optimized for each adsorption site calculation.

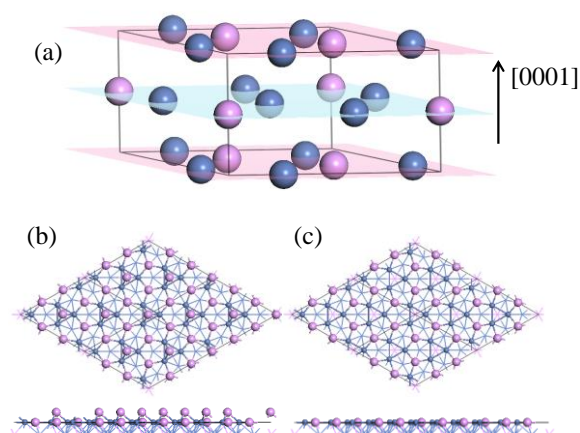


Figure 1. (a) Bulk Structure of Ni₂P. Structure model of two types of Ni₂P(0001) surface (b) Ni₃PP and (c) Ni₃P₂. Pink ball: Phosphorus, blue ball: Ni.

On both Ni₃PP and Ni₃P₂ surfaces, many possible adsorption sites give the positive adsorption energies. The most stable

Ni-P: bridge site of Ni and P

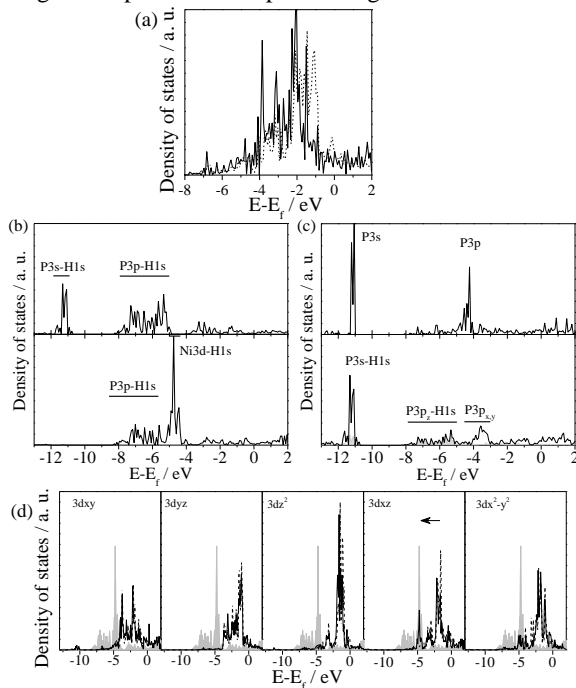
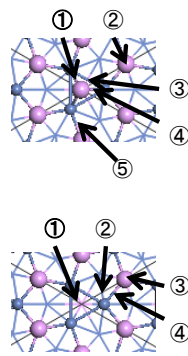


Figure 2. (a) Density of states (DOS) of a Ni of Ni trimer on surface before (Ni₃P₂ (dotted line)) and after (Ni₃PP(solid line)) the P coverage. (b) DOS of hydrogen adsorbed on Ni₃PP (upper) and Ni₃P₂ (lower) surfaces. (c) DOS of topmost phosphorus on the Ni₃PP surface before (upper) and after (lower) hydrogen adsorption. Gray filled regions indicate hydrogen DOS. (d) Projected DOS of Ni 3d in the Ni trimer on Ni₃P₂ surface before (solid line) and after (dotted line) hydrogen adsorption. Gray filled regions indicate hydrogen DOS.

Table 1. Adsorption energy of hydrogen on Ni₂P(0001) surface

Surface	Site of hydrogen	E _{ads} / eV
Ni ₃ PP	1. P _{top}	-0.22
	2. P _{second}	0.15
	3. NiNiP	0.31
	4. NiP _{top}	-0.04
	5. NiP _{second}	0.23
Ni ₃ P ₂	1. Ni _{tri}	-0.65
	2. Ni _{atop}	-0.01
	3. P	0.09
	4. Ni-P	-0.05



For Ni₃PP

1. P_{top}: atop site of the topmost P of Ni₃PP.
2. P_{second}: atop site of the second layer P.
3. NiNiP: three fold site composed of topmost P and two 2nd layer Ni atoms
4. NiP_{top}: bridge site of topmost P and 2nd layer Ni.
5. NiP_{second}: bridge site of 2nd layer Ni and 2nd layer P. as shown in the upperfigure

For Ni₃P₂

1. Ni_{tri}: three fold site of Ni trimer
2. Ni_{atop}: atop site of Ni atom.
3. P: atop site of P atom

sites for Ni₃PP and Ni₃P₂ surfaces are atop site of phosphorus (-0.20 eV) and three fold hollow site of surface Ni trimer (-0.65 eV), respectively. The hydrogen adsorption site and the adsorption energy for Ni₃P₂ surface are consistent with the previous report.[3] The adsorption energy of hydrogen was also comparable with that adsorbed on Ni(111) surface, which are typical values for transition metal surfaces.[22] It is quite interesting that the surface phosphorus of Ni₃PP can be the adsorption site even though the phosphorus is usually regarded as poison.

Figure 2(b) shows the DOS of hydrogen adsorbed on Ni₃PP(upper) and Ni₃P₂(lower). Figure 2(c) shows the DOS of phosphorus before(upper) and after(lower) the hydrogen adsorption on Ni₃PP surface. The DOS for phosphorus 3s and 3p_z on Ni₃PP shows rather sharp peaks around -11 eV and -4.2 eV, respectively before the hydrogen adsorption. The DOS of phosphorus largely changed with the adsorption of hydrogen as shown in the lower panel of Figure 2(c). The Gray-filled region is the hydrogen DOS which is rescaled from the upper frame of Figure 2(b) to level the DOS of phosphorus. The DOS for 3s and 3p_z of phosphorus appear at the same energy position of those of hydrogen 1s, indicating that the major contributions to the P-H bonding arise from phosphorus 3s orbitals around -11 eV and phosphorus 3p_z orbitals in the energy range of -4.9 to -8.3 eV(-6.7 eV in average) Note that the 3p_z orbital of phosphorus is stabilized with hydrogen adsorption by about 2.5 eV in average. On the other hand, the characteristic features of hydrogen DOS on Ni₃P₂ are sharp peak at -4.7 eV and broad band in the energy range of -5.2 to -8.4 eV. Figure 2(d) shows projected DOS of a Ni atom of Ni trimer below the hydrogen on the Ni₃P₂ surface. The x-axis of each d orbital of Ni atoms is taken in the direction of Ni-H bonding projected onto the surface. The sharp peak at -4.7 eV corresponds to a bonding between hydrogen 1s orbital and Ni 3d_{xz} orbital. Before the adsorption of hydrogen the PDOS of the 3d_{xz} appears at -1.6 eV(dotted line). The bonding stabilizes Ni 3d_{xz} orbital by 3.1 eV (Figure 2(d)).

These bondings are shown in the energy-band decomposed charge density in Figure 3 to visualize the real space bonding feature. The P(3s)-H covalent bonding in Figure 3(a) and P(3p_z)-H bonding in Figure 3(b) correspond to bonding of hydrogen 1s orbital and topmost phosphorus 3s and 3p_z orbital on hydrogen adsorbed Ni₃PP surface, respectively. The hydrogen adsorption occurs on Ni₃P₂ surface with P(3p_z)-H bonding in Figure 3(c) and Ni (3d_{xz})-H bonding in Figure 3(d).

Comparing the hydrogen species adsorbed on Ni₃PP and Ni₃P₂ surfaces, the latter hydrogen has 3 times higher adsorption energy than the former hydrogen. The stabilization of Ni trimer 3d orbitals causes the stronger Ni-H interaction, which suggests the 3 fold hollow site of Ni trimer may be catalytically active, while phosphorus covered area is rather passivated. Since the 80 % of surface is covered by phosphorus, the surface requires further activation to provide catalytically active surface. We are now trying to reveal the effect of sulfur on the same surface which is claimed to be formed during the reaction condition and to be the candidate for the active site structure.[12,13]

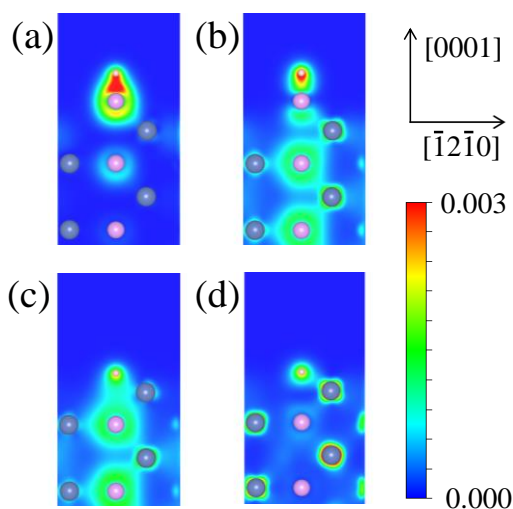


Figure 3. The band decomposed charge density of hydrogen adsorbed Ni₃PP surface in the energy range of (a) -14.0 to -10.0 eV and (b) -8.5 to -5.0 eV. Those of hydrogen adsorbed Ni₃P₂ surface in the energy range of (c) -8.6 to -6.0 eV and (d) -5.5 to -4.0 eV (isosurface: 0.03). Blue part: electron depression, yellow part: electron accumulation. Large pink ball: Phosphorus, large blue ball: Ni, small ball: Hydrogen.

In conclusion, we compared hydrogen adsorption energies and electronic states on two different surface structures of Ni₂P(0001), such as Ni₃PP and Ni₃P₂ surface. The presence of surface phosphorus in Ni₃PP stabilized Ni₂P surface by forming the P-Ni bond. Hydrogen adsorption energy on Ni₃P₂ surface was larger than Ni₃PP surface. Electronic states analysis shows the major factors for difference come from high instability of Ni trimer exposed on the Ni₃P₂ surface. Modification of surface is necessary to expose catalytic active surface, since 80 % of Ni₂P(0001) surface is covered by Ni₃PP surface.

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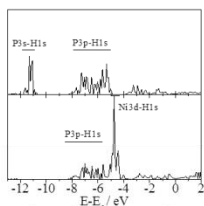
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Graphical Information



Ni₃PPH
on Ni₂P (0001)

