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# Density function theoretical investigation on the Ni<sub>3</sub>PP structure and its hydrogen adsorption property of Ni<sub>2</sub>P(0001) surface

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Electronic and structural properties of phosphorus terminated structure of Ni<sub>2</sub>P(0001) surface (Ni<sub>3</sub>PP) are investigated by density functional theoretical (DFT) calculation. Phosphorus adsorption largely stabilizes the Ni<sub>2</sub>P(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 Ni<sub>3</sub>P<sub>2</sub> surface. Our results suggest that the Ni trimer is the key factor for high catalytic activity.

Nickel phosphide (Ni<sub>2</sub>P) 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 Ni<sub>2</sub>P surface in an atomic level. The bulk structure of Ni<sub>2</sub>P is composed of two different layers with different composition, Ni<sub>3</sub>P<sub>2</sub> and Ni<sub>3</sub>P<sub>1</sub>, aligning alternately along the [0001] direction as shown in Figure 1(a). Rodriguez et al. showed that Ni<sub>3</sub>P<sub>2</sub> surface was more stable surface than Ni<sub>3</sub>P<sub>1</sub> surface and they discussed the hydrogen adsorption properties on the Ni<sub>3</sub>P<sub>2</sub> surface.[3] However, scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) studies on the Ni<sub>2</sub>P(0001) have revealed that the Ni<sub>2</sub>P(0001) surface is mainly (about 80 %) covered with phosphorus on the Ni three fold site of Ni<sub>3</sub>P<sub>2</sub> surface after 953 K annealing under UHV conditions with minor amount of uncovered Ni<sub>3</sub>P<sub>2</sub> surface.[4-6] This new phosphorus covered surface is called as Ni<sub>3</sub>PP 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 Ni<sub>2</sub>P creates the active phase.[11-13] Therefore the chemically modified Ni<sub>2</sub>P 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 Ni<sub>3</sub>PP surface to reveal the mechanism of P-covered surface formation and its hydrogen adsorption properties in comparison with the Ni<sub>3</sub>P<sub>2</sub>.

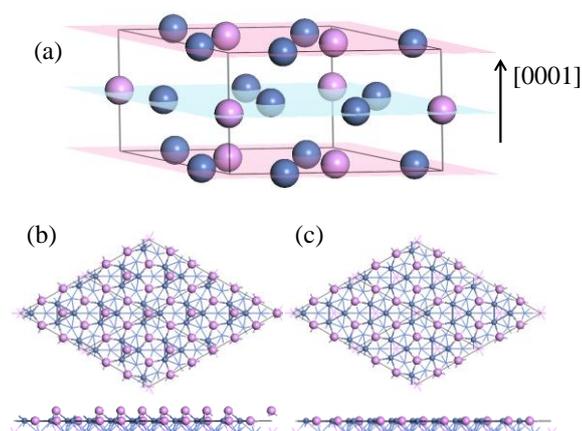
DFT calculations were performed using the Vienna ab-initio Simulation Package code (VASP 5.2.12).[14-16] The Perdew-Burke-Ernzerh exchange-correlation functional with a generalized gradient approximation [17,18] was used. Projector-augmented wave approach (PAW) [19,20] have been used together with plane wave basis sets. The optimized bulk Ni<sub>2</sub>P lattice constants were  $a = b = 0.5876$  nm,  $c = 0.3365$  nm,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ . The Ni<sub>2</sub>P(0001) surface was modeled with 12 atomic-layers periodic slab with a ca. 3.5 nm vacuum layer. The chemical formula of Ni<sub>3</sub>P<sub>2</sub> and Ni<sub>3</sub>PP are Ni<sub>36</sub>P<sub>18</sub> and Ni<sub>36</sub>P<sub>19</sub>, 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 Ni<sub>3</sub>PP and Ni<sub>3</sub>P<sub>2</sub> 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 Ni<sub>3</sub>P<sub>2</sub> 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 Ni<sub>3</sub>P<sub>2</sub> 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 Ni<sub>3</sub>PP structure is created. On the other hand DOS of P on the topmost Ni<sub>3</sub>P<sub>2</sub> 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 Ni<sub>3</sub>PP.

We calculated the hydrogen adsorption energy and electronic state of Ni<sub>3</sub>PP surface. Table 1 summarizes the adsorption energies of atomic hydrogen on both surfaces, Ni<sub>3</sub>PP and Ni<sub>3</sub>P<sub>2</sub>. Surface energies were calculated by following expression:

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

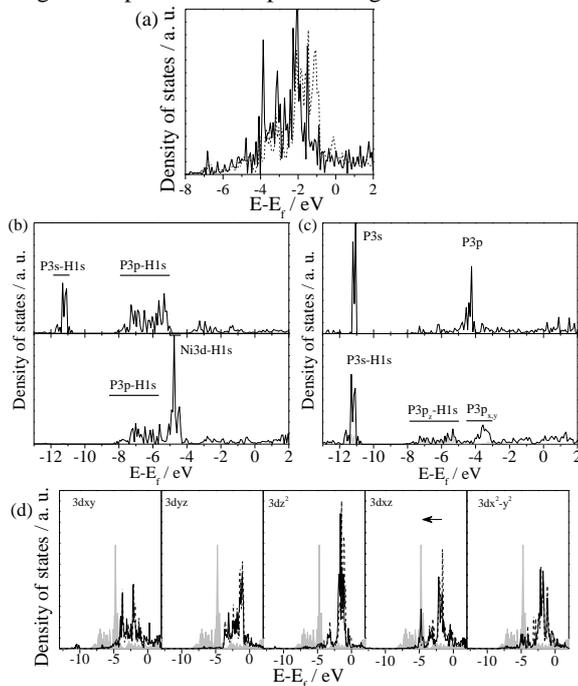
were  $E_{H+Ni_2P}$ ,  $E_{H_2}$  and  $E_{Ni_2P}$  correspond to total energy of hydrogen adsorbed on Ni<sub>2</sub>P, isolated hydrogen molecule and isolated surface, respectively. Both hydrogen and surface structures are optimized for each adsorption site calculation.



**Figure 1.** (a) Bulk Structure of Ni<sub>2</sub>P. Structure model of two types of Ni<sub>2</sub>P(0001) surface (b) Ni<sub>3</sub>PP and (c) Ni<sub>3</sub>P<sub>2</sub>. Pink ball: Phosphorus, blue ball: Ni.

On both Ni<sub>3</sub>PP and Ni<sub>3</sub>P<sub>2</sub> surfaces, many possible adsorption sites give the positive adsorption energies. The most stable

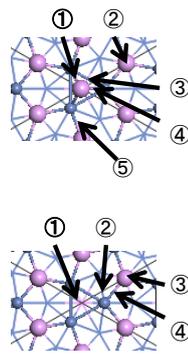
Ni-P: bridge site of Ni and P



**Figure 2.** (a) Density of states (DOS) of a Ni of Ni trimer on surface before (Ni<sub>3</sub>P<sub>2</sub> (dotted line) ) and after (Ni<sub>3</sub>PP(solid line)) the P coverage. (b) DOS of hydrogen adsorbed on Ni<sub>3</sub>PP (upper) and Ni<sub>3</sub>P<sub>2</sub> (lower) surfaces. (c) DOS of topmost phosphorus on the Ni<sub>3</sub>PP 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 Ni<sub>3</sub>P<sub>2</sub> surface before (solid line) and after (dotted line) hydrogen adsorption. Gray filled regions indicate hydrogen DOS.

**Table 1.** Adsorption energy of hydrogen on Ni<sub>2</sub>P(0001) surface

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



For Ni<sub>3</sub>PP

1. P<sub>top</sub>: atop site of the topmost P of Ni<sub>3</sub>PP.
2. P<sub>second</sub>: atop site of the second layer P.
3. NiNiP: three fold site composed of topmost P and two 2<sup>nd</sup> layer Ni atoms
4. NiP<sub>top</sub>: bridge site of topmost P and 2<sup>nd</sup> layer Ni.
5. NiP<sub>second</sub>: bridge site of 2<sup>nd</sup> layer Ni and 2<sup>nd</sup> layer P. as shown in the upperfigure

For Ni<sub>3</sub>P<sub>2</sub>

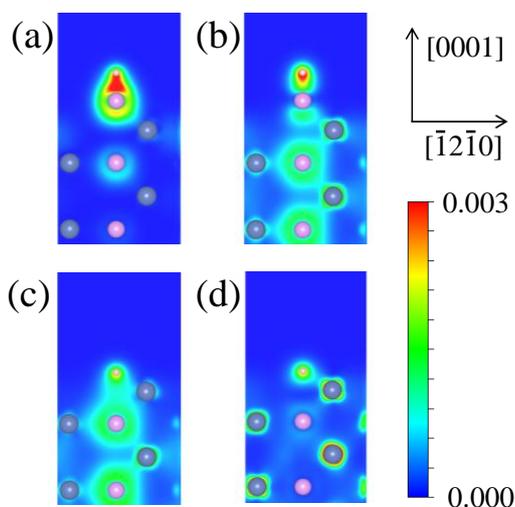
1. Ni<sub>tri</sub>: three fold site of Ni trimer
2. Ni<sub>atop</sub>: atop site of Ni atom.
3. P: atop site of P atom

sites for Ni<sub>3</sub>PP and Ni<sub>3</sub>P<sub>2</sub> 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 Ni<sub>3</sub>P<sub>2</sub> 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 Ni<sub>3</sub>PP can be the adsorption site even though the phosphorus is usually regarded as poison.

Figure 2(b) shows the DOS of hydrogen adsorbed on Ni<sub>3</sub>PP(upper) and Ni<sub>3</sub>P<sub>2</sub>(lower). Figure 2(c) shows the DOS of phosphorus before(upper) and after(lower) the hydrogen adsorption on Ni<sub>3</sub>PP surface. The DOS for phosphorus 3s and 3p<sub>z</sub> on Ni<sub>3</sub>PP 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<sub>z</sub> 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<sub>z</sub> orbitals in the energy range of -4.9 to -8.3 eV(-6.7 eV in average) Note that the 3p<sub>z</sub> 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 Ni<sub>3</sub>P<sub>2</sub> 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 Ni<sub>3</sub>P<sub>2</sub> 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<sub>xz</sub> orbital. Before the adsorption of hydrogen the PDOS of the 3d<sub>xz</sub> appears at -1.6 eV(dotted line). The bonding stabilizes Ni 3d<sub>xz</sub> 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<sub>z</sub>)-H bonding in Figure 3(b) correspond to bonding of hydrogen 1s orbital and topmost phosphorus 3s and 3p<sub>z</sub> orbital on hydrogen adsorbed Ni<sub>3</sub>PP surface, respectively. The hydrogen adsorption occurs on Ni<sub>3</sub>P<sub>2</sub> surface with P(3p<sub>z</sub>)-H bonding in Figure 3(c) and Ni (3d<sub>xz</sub>)-H bonding in Figure 3(d).

Comparing the hydrogen species adsorbed on Ni<sub>3</sub>PP and Ni<sub>3</sub>P<sub>2</sub> 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 Ni<sub>3</sub>PP 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 Ni<sub>3</sub>P<sub>2</sub> 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 Ni<sub>2</sub>P(0001), such as Ni<sub>3</sub>PP and Ni<sub>3</sub>P<sub>2</sub> surface. The presence of surface phosphorus in Ni<sub>3</sub>PP stabilized Ni<sub>2</sub>P surface by forming the P-Ni bond. Hydrogen adsorption energy on Ni<sub>3</sub>P<sub>2</sub> surface was larger than Ni<sub>3</sub>PP surface. Electronic states analysis shows the major factors for difference come from high instability of Ni trimer exposed on the Ni<sub>3</sub>P<sub>2</sub> surface. Modification of surface is necessary to expose catalytic active surface, since 80 % of Ni<sub>2</sub>P(0001) surface is covered by Ni<sub>3</sub>PP surface.

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## Graphical Abstract

### Textual Information

Description (if any)

DOS of phosphorus before and after the hydrogen adsorption

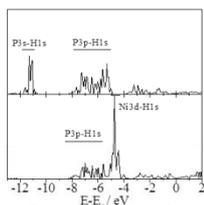
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### Graphical Information



Ni<sub>3</sub>PPH  
on Ni<sub>2</sub>P (0001)

