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Density functional theoretical investigation on the \( \text{Ni}_3\text{PP} \) structure and its hydrogen adsorption property of \( \text{Ni}_3\text{P}(0001) \) surface

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Electronic and structural properties of phosphorous terminated structure of \( \text{Ni}_3\text{P}(0001) \) surface (\( \text{Ni}_3\text{PP} \)) are investigated by density functional theoretical (DFT) calculation. Phosphorus adsorption largely stabilizes the \( \text{Ni}_3\text{P}(0001) \) 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 \( \text{Ni}_3\text{P}_2 \) surface. Our results suggest that the Ni trimer is the key factor for high catalytic activity.

Nickel phosphide \( (\text{Ni}_3\text{P}) \) shows a high catalytic activity for the hydrodesulfurization[1] and other hydrorefining catalysts towards hydrogenation and hydrodeoxygenation and so on.[2] The key issue to understand the hydrogenation reactions is interaction between hydrogen with \( \text{Ni}_3\text{P} \) surface in an atomic level. The bulk structure of \( \text{Ni}_3\text{P} \) is composed of two different layers with different composition, \( \text{Ni}_3\text{P}_2 \) and \( \text{Ni}_3\text{P}_1 \), aligning alternately along the [0001] direction as shown in Figure 1(a). Rodriguez et al. showed that \( \text{Ni}_3\text{P}_2 \) surface was more stable surface than \( \text{Ni}_3\text{P}_1 \) surface and they discussed the hydrogen adsorption properties on the \( \text{Ni}_3\text{P}_2 \) surface.[3] However, scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) studies on the \( \text{Ni}_3\text{P}(0001) \) have revealed that the \( \text{Ni}_3\text{P}(0001) \) surface is mainly (about 80 %) covered with phosphorus on the Ni three fold site of \( \text{Ni}_3\text{P}_2 \) surface after 953 K annealing under UHV conditions with minor amount of uncovered \( \text{Ni}_3\text{P}_2 \) surface.[4-6] This new phosphorus covered surface is called as \( \text{Ni}_3\text{PP} \) 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 \( \text{Ni}_3\text{P} \) creates the active phase.[11-13] Therefore the chemically modified \( \text{Ni}_3\text{P} \) 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 \( \text{Ni}_3\text{PP} \) surface to reveal the mechanism of P-covered surface formation and its hydrogen adsorption properties in comparison with the \( \text{Ni}_3\text{P}_2 \).

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 \( \text{Ni}_3\text{P} \) lattice constants were \( a = b = 0.5876 \) nm, \( c = 0.3365 \) nm, \( \alpha = \beta = 90^\circ, \gamma = 120^\circ \). The \( \text{Ni}_3\text{P}(0001) \) surface was modeled with 12 atomic-layers periodic slab with a ca. 3.5 nm vacuum layer. The chemical formula of \( \text{Ni}_3\text{P}_2 \) and \( \text{Ni}_3\text{PP} \) are \( \text{Ni}_{18}\text{P}_{18} \) and \( \text{Ni}_{18}\text{P}_{19} \), 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 the \( \text{Ni}_3\text{P} \) and \( \text{Ni}_3\text{PP} \) 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 \( \text{Ni}_3\text{P}_2 \) 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-removed \( \text{Ni}_3\text{P}_2 \) surface which are assigned to 3d states. The peak at -0.5 eV has a spread crossing the Fermi level. They are shifted down to the band between -1.5 and -4.5 eV and the peak at -3.9 eV by the interaction with phosphorus when the \( \text{Ni}_3\text{PP} \) structure is created. On the other hand DOS of P on the topmost \( \text{Ni}_3\text{P}_2 \) 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 \( \text{Ni}_3\text{PP} \).

We calculated the hydrogen adsorption energy and electronic state of \( \text{Ni}_3\text{PP} \) surface. Table 1 summarizes the adsorption energies of atomic hydrogen on both surfaces, \( \text{Ni}_3\text{P} \) and \( \text{Ni}_3\text{PP} \). Surface energies were calculated by following expression:

\[ E_{ad} = E_{H+Ni_{3}P} - \left( \frac{1}{2} E_{H_2} + E_{Ni_{3}P} \right) , \]

where \( E_{H_{Ni_{3}P}}, E_{H_2} \) and \( E_{Ni_{3}P} \) correspond to total energy of hydrogen adsorbed on \( \text{Ni}_3\text{P} \), isolated hydrogen molecule and isolated surface, respectively. Both hydrogen and surface structures are optimized for each adsorption site calculation.

![Figure 1](image-url)
On both Ni3PP and Ni3P2 surfaces, many possible adsorption sites give the positive adsorption energies. The most stable

![Density of states](image)

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 (solid line) and after (dotted line) hydrogen adsorption. Gray filled regions indicate hydrogen DOS.

Table 1. Adsorption energy of hydrogen on Ni3P(0001) surface

<table>
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<tr>
<th>Surface</th>
<th>Site of hydrogen</th>
<th>E_ads / eV</th>
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<tbody>
<tr>
<td>Ni3PP</td>
<td>1. Ptop</td>
<td>-0.22</td>
</tr>
<tr>
<td></td>
<td>2. Psecond</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>3. NiNIP</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>4. NiP3d</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>5. NiP3s</td>
<td>0.23</td>
</tr>
<tr>
<td>Ni3P2</td>
<td>1. Ntop</td>
<td>-0.65</td>
</tr>
<tr>
<td></td>
<td>2. Nsecond</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td>3. P</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>4. Ni-P</td>
<td>-0.05</td>
</tr>
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For Ni3PP
1. Ptop: atop site of the topmost P of Ni3PP.
2. Psecond: atop site of the second layer P.
3. NiNIP: three fold site composed of topmost P and two 2nd layer Ni atoms.
5. NiP3s: bridge site of 2nd layer Ni and 3rd layer P. As shown in the upperfigure.

For Ni3P2
1. Ntop: three fold site of Ni trimer.

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 fo Ni3P2 surface are consistent with the previous report.[3] The adsorption energy of hydrogen was also comparable with that adsorbed on Ni(N111) 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 on Ni3PP shows rather sharp peaks around -11 eV and -4.2 eV, respectively before the hydrogen adsorption. The DOS for 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, 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 orbitals in the energy range of -4.9 to -8.3 eV (-6.7 eV in average). Note that the 3p 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 (PDOS) 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 3dz orbital. Before the adsorption of hydrogen the PDOS of the 3dx appears at -1.6 eV (dotted line). The bonding stabilizes Ni 3dz 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)-H bonding in Figure 3(b) correspond to bonding of hydrogen 1s orbital and topmost phosphorus 3s and 3p orbital on hydrogen adsorbed Ni3PP surface, respectively. The hydrogen adsorption occurs on Ni3P2 surface with P(3p)-H bonding in Figure 3(c) and Ni (3dσ)-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]
In conclusion, we compared hydrogen adsorption energies and electronic states on two different surface structures of Ni$_3$P(0001), such as Ni$_3$PP and Ni$_3$P$_2$ surface. The presence of surface phosphorus in Ni$_3$PP stabilized Ni$_3$P surface by forming the P-Ni bond. Hydrogen adsorption energy on Ni$_3$P$_2$ surface was larger than Ni$_3$PP surface. Electronic states analysis shows the major factors for difference come from high instability of Ni trimer exposed on the Ni$_3$P$_2$ surface. Modification of surface is necessary to expose catalytic active surface, since 80 % of Ni$_3$P(0001) surface is covered by Ni$_3$PP surface.

References and Notes
The diagram is acceptable in a colored form. Publication of the colored figures are free of charge.

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If the data of your G.A. is "bit-mapped image" data (not "vector data"), note that its print-resolution should be 300 dpi.

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