



Title	An Investigation of Ni ₂ P Single Crystal Surfaces : Structure, Electronic State and Reactivity
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Citation	Topics in catalysis, 58(4-6), 194-200 https://doi.org/10.1007/s11244-015-0360-6
Issue Date	2015-04
Doc URL	https://hdl.handle.net/2115/61040
Rights	The final publication is available at link.springer.com
Type	journal article
File Information	Ni ₂ P_Review_Yuan_1126-1.pdf



An Investigation of Ni₂P Single Crystal Surfaces: Structure, Electronic State and Reactivity

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Abstract

Ni₂P has demonstrated high catalytic activity for hydrodesulfurization and has recently been employed as a catalyst in a variety of other reactions. We have thoroughly reviewed the literature concerning Ni₂P single crystal surfaces, with the aim of determining the relationship between surface structure and catalytic properties. Published results to date indicate that Ni₂P single crystal surfaces exhibit reconstructed structures, and so the bulk terminated structure may not be stable. We have also reviewed the surface structures and electronic states of (1×1) and reconstructed Ni₂P (0001) and (10 $\bar{1}$ 0). Based on these reviews, this paper presents general rules regarding stabilization of the Ni₂P surface structure and discusses the role of phosphorus in the single crystal surfaces.

Keywords: single crystal surfaces, nickel phosphide, electronic structure, surface structure, scanning tunneling microscopy, density functional theory, LEED IV

1. Introduction

Recent legislation requires the removal of sulfide compounds from fuels as a means of reducing environmental pollution[1]. As a result, there is a demand for new hydrotreating catalysts and also a need to improve current hydrodesulfurization (HDS) catalysts, such as Ni and Co-promoted MoS₂ or WS₂ [2]. Noble metals such as Pt and Pd have shown high activity in this regard [3], but the high cost of these materials often prohibits their industrial applications. Transition metal phosphides (TMPs) represent an alternative and are considered to have potential as hydrotreating catalysts, since they exhibit superior catalytic activity during HDS compared to conventional catalysts. Among the TMPs, the high activity and thermostability of Ni₂P makes it an ideal catalyst for HDS [4-7]. Ni₂P can also serve as a catalyst for other hydrotreating reactions, such as hydrodenitrogenation [4,5,8] and hydrodeoxygenation [9,10], as well as for hydrogen evolution reactions (HERs) [11, 12], dehydrogenation of cyclohexane[13] and water-gas-shift (WGS) reactions [14]. In HDS, the Ni atoms are

active sites though Ni atoms in pure Ni metal particles bond strongly with S, which tends to reduce the catalytic activity. The P sites in Ni₂P are thought to play several crucial roles in the catalytic process. The weak ligand effect introduced by P sites helps to stabilize the Ni 3d level. In addition, the presence of P dilutes the density of the active Ni sites and thus reduces deactivation of the surface by S poisoning (an ensemble effect) [15]. In addition Oyama et al. found that the NiPS phase are active for hydrodesulfurization reaction and they suggested the Ni(2) provides active site. [16-21]

Despite these current insights, a thorough understanding of the high activity of Ni₂P at the atomic level requires us to investigate the structures and properties of Ni₂P single crystals. Many efforts have been made to date to elucidate the surface properties of Ni₂P single crystal surfaces, using X-ray photoelectron spectroscopy (XPS) [22,23], scanning tunneling microscopy (STM) [24-28], low-energy electron diffraction (LEED) [24-30], photoemission electron microscopy (PEEM) [25], photoelectron diffraction [31] and photoemission spectroscopy (PES) [30,32-35]. Theoretical calculations using density functional theory (DFT) [11,14,15,36-38] have also played an important role in understanding the catalytic properties of the surface. These studies have indicated that the Ni₂P single crystal surface is stabilized by reordering of the P atoms. In this review paper, we survey the available literature concerning the surface structure and electronic state of Ni₂P single crystals and attempt to elucidate the key factors that stabilize the surface structure and activate the Ni₂P surfaces.

2. Synthesis of a Ni₂P single crystal

The Ni-P phase diagram incorporates several phases, including Ni₁₂P₅, Ni₃P, Ni₂P, NiP and NiP₂[39], and therefore careful preparation is required to obtain Ni₂P as a single phase. Otani et al. applied the floating zone method to Ni₂P single crystal synthesis [40], in which Ni₂P powder was isostatically pressed at 200 MPa and heated to 1073 K to obtain a sintered rod. This rod was subsequently heated by radio frequency and experienced a growth rate of 1 cm/h under 0.4 MPa of Ar. The resulting single crystal grew primarily along the [0001] direction. Chemical analyses using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and structural analysis by X-ray diffraction indicated that the stoichiometry and lattice constants of the synthesized crystal were consistent with those of Ni₂P.

3. Surface structures, electronic states and reactivities of Ni₂P single crystal surfaces.

3.1 Crystal structure of Ni₂P

Bulk Ni₂P has an orthorhombic structure and belongs to the space group $P\bar{6}_2m$ [41], with lattice parameters $a = 0.5859$ nm and $c = 0.3382$ nm, as shown in Fig. 1. In this structure, there are two different types of P atoms, P(1) and P(2), as well as two types of Ni atoms, Ni(1) and Ni(2) as shown in Fig.1. The P(1) and P(2) atoms are located at the 1b and 2c sites, respectively. There are four P atoms surrounding each Ni(1) atom at the 3f sites in a near-tetrahedral manner, producing Ni-P distances of 0.221 (with two P(2)) and 0.227 (with two P(1)) nm. The Ni(2) atoms are located at the 3g sites, surrounded by five P atoms in a square pyramidal structure, in which one Ni-P bond is 0.237 nm with P(1) and the remaining four Ni-P bonds are 0.256 nm with P(2). The crystal can be described as being composed of two inequivalent layer structures, designated Ni₃P and Ni₃P₂, stacked alternatively along the [0001] direction. These two structures give an average stoichiometry of Ni₂P. The Ni₃P layer is composed of Ni(2) and P(1) atoms while the Ni₃P₂ layer is composed of Ni(1) and P(2) atoms.

3.2 Ni₂P (0001)

DFT calculations have shown that the Ni₃P₂-terminated surface is more stable than the Ni₃P-terminated surface [15,38]. Moula et al. first obtained atomic-scale resolution STM images of a Ni₂P(0001) surface [24-26]. In this work, two types of (1×1) STM images were acquired under a positive potential bias, after annealing up to 970 K for 5 h. Due to the higher local density of states associated with P within the potential range of the STM voltage bias applied in the Moula study, the two types of STM images were assumed to indicate the P atoms on Ni₃P-terminated and Ni₃P₂-terminated surfaces, respectively. First principles calculations conducted by Li and Hu taking the chemical potential changes into account also agreed with this assignment, though they showed that the total internal energy of the Ni₃P₂ surface itself is lower than that of the Ni₃P surface [38].

Hernandez et al. carried out a dynamical LEED analysis of I-V curves [29,42] obtained from a Ni₂P(0001)-(1×1) surface, and found that simple bulk-terminated (1×1) structures, whether Ni₃P or Ni₃P₂-terminated, could not account for the experimental data. They therefore considered other models in which Ni or P atoms were depleted from the surface while maintaining the (1×1) symmetry. Four such models were found to be possible, as shown in Fig. 2 [29]. By comparing each of these four proposed models of the surface with the experimental LEED I-V curves, it was concluded that the (0001) surface was primarily terminated with the P-covered Ni₃P₂ (Ni₃P-P) structure shown in Fig. 3. In this structure, P adatoms stabilize the surface by bonding with the dangling bonds of three-fold Ni atoms [36]. Further analysis showed that the Ni₃P-P

structure accounts for $80\pm 10\%$ of the total surface, while the remainder (about 20%) is composed of an uncovered Ni_3P_2 structure [29]. This model structure therefore explains the apparent contradiction between theoretical predictions [15] and experimental STM images [24-26]. Edamoto et al. investigated the electronic structure of $\text{Ni}_2\text{P}(0001)-(1\times 1)$ using angle-resolved photoelectron spectroscopy (ARPES) [32,33,35] and observed a Ni 3d-P 3p hybrid band (determined to be the main band) around 0-4 eV and a satellite band at 8 eV in the photoelectron(PE) spectra. The satellite band was attributed to the two-hole bound state resulting from the resonance behavior of the Ni 3d photoemission. In addition, a peak shifted towards lower energy compared to the bulk material was observed in the P 2p PE peak, indicating that the P atoms were negatively charged.

The $\text{Ni}_2\text{P}(0001)$ surface has been reconstructed to give several structures, including $(2/3\times 2/3)$, which was observed almost at the same preparation condition as the (1×1) structure but seemingly at a little higher temperature.[26]. Kinoshita et al. reported a reconstructed $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure for $\text{Ni}_2\text{P}(0001)$ after annealing at 790 K based on the analysis by LEED and low-temperature STM [27]. Low temperature STM images of this material showed a framework composed of propeller-like structures with both filled and empty sites.

Only a few studies have examined the catalytic properties of the Ni_2P single crystal surface, although the application of this surface to HDS, HER and WGS has been examined with both experimental and theoretical methods. The active sites for each reaction on $\text{Ni}_2\text{P}(0001)$ surface are summarized in Table 1. Liu et al. studied desulfurization using XPS data and DFT calculations [15] and determined from the XPS results that thiophene, which is the most common HDS test molecule, readily dissociated on a $\text{Ni}_2\text{P}(0001)-(1\times 1)$ surface at approximately 200 K. This was of note since the rate limiting step of the desulfurization reaction is the removal of adsorbed S (S_{ad}) by hydrogen, which normally takes place above 600 K. The XPS data also revealed that exposure of the crystal surface to low concentrations of S_2 gas (created from the decomposition of Ag_2S [15]) generates S adatoms that remain firmly bound to the crystal surface up to a temperature of 700 K. In contrast, S adatoms on a S-saturated surface desorb at 400 to 450 K. DFT calculations conducted on the Ni_3P_2 -terminated surface demonstrated that S bonds to the surface at two sites, in Ni 3-fold hollow sites, at which the S is more stable, and to Ni-P bridges, where the S bonding energy is lower than at the Ni 3-fold hollow sites. The bonding energy of S on $\text{Ni}_2\text{P}(0001)$ was also found to decrease with increasing surface coverage by S. This occurs since S adatoms initially bond to Ni 3-fold hollow sites, at which the S bonding energy is higher. With increasing exposure to S, however, these sites became saturated and so more S adatoms

bonded to the Ni-P bridges, decreasing the temperature required for desorption of S. This property makes the Ni₂P surface a good candidate for HDS. In addition, since the P atoms possess a slight negative charge (-0.07e), they provide additional sites for hydrogen adsorption [15,36]. This theoretical proposal has also been supported by studies of the electronic structure of Ni₂P [35]. Liu et al. examined the electrocatalytic properties of Ni₂P(0001) during HER using DFT calculations [11] and determined that Ni₂P(0001) has the potential for high HER activity. H-poisoning of the surface was found to enhance the reaction kinetics, due to the weak adsorption of H* at the Ni-P bridge sites adjacent to strong adsorption sites and the corresponding reductions in the recombination and desorption activation energies. WGS was also studied by the same group [14]. The activity of Ni₂P(0001) was comparable to that of commercial WGS catalysts such as Cu, and Ni₂P(0001) also exhibited high thermostability. The bonding energies of the adsorption species are reduced on the oxygen covered Ni₂P(0001) surface. DFT study of HDO revealed that 3-fold hollow Ni and P sites are active for adsorption of H and OH species [43]. Different from the above mentioned studies based on Ni₃P₂-terminated surface, which is more stable than Ni₃P-terminated surface, dissociative adsorption of hydrogen was found on Ni₃P-terminated surface [25]. In contrast, Miyamoto used thermal desorption spectroscopy (TDS) to demonstrate experimentally that pure Ni₂P(0001) is inactive for the adsorption of molecules and that thiophene and molecular hydrogen adsorption on the surface must be stimulated through excitation of the molecules via an ionization gauge filament [44]. This inertness of Ni₂P(0001) surface can be explained by the coverage of P atoms, since 80% of the Ni₂P(0001)-(1×1) surface is terminated with Ni₃P-P surface, where the active Ni sites are covered by P [29].

3.3 Ni₂P(10 $\bar{1}$ 0)

In the Ni₂P crystal structure, there are two different layers stacked along the [0001] direction in an ABBABB fashion, where A and B correspond to different P positions within the same Ni₂P composition. Guo et al. examined the Ni₂P surface using STM and LEED [28]. After annealing at 573 K, the surface presented a (1×1) structure, while a reconstructed c(2×4) structure appeared by the following annealing at 723 K. Both structures were observed by STM in the reconstructed c(2×4) structure. Similar to the (0001) surface, protrusions were observed and were attributed to P sites, a speculation subsequently confirmed by DFT calculations. A Ni-missing row and a P-added row (MRARM) model were proposed to describe the reconstructed STM image, as shown in Fig. 4. Edamoto also studied the electronic structure of the reconstructed (10 $\bar{1}$ 0)-c(2×4)

surface [34,35] and found it resembled the (0001) plane. In the valence band of this structure, a main Ni 3d-P 3p hybrid band and a satellite band were observed at 0-4 and 8 eV, respectively. Just as in the $\text{Ni}_2\text{P}(0001)-(1\times 1)$ PES, this satellite band was determined to be related to the photoemission process resulting from a two-hole bound state. An additional peak was evident at 0.6 eV, attributed to a surface state (mainly composed of P 3p) having a small dispersion along the [0001] direction of the $c(2\times 4)$ structure. As noted above and shown in Fig. 4, a zigzag-shaped P chain is present in the MRARM structure in the uppermost portion of the surface. Thus, the peak observed at 0.6 eV is a consequence of the P zigzag chain structure. Kono et al. used STM images to find another reconstructed structure, corresponding to a $c(2\times 2)$ surface, together with the previously determined $c(2\times 4)$ structure, as shown in Fig. 5 [45]. They proposed a structural model for $\text{Ni}_2\text{P}(10\bar{1}0)$ that incorporated these reconstructed structures, as shown in Fig. 4 [45]. Kono et al. also studied the surface reactivity of reconstructed $\text{Ni}_2\text{P}(10\bar{1}0)$ with NO and determined that only a $c(2\times 4)$ surface with an adjacent (1×1) structure reacted with NO, while a $c(2\times 4)$ surface with a neighboring $c(2\times 2)$ domain was unreactive. Adsorption of NO was not observed on Ni_2P surface while a NO adsorption was found on W modified Ni_2P surface. [31]

4. The role of phosphorus

S.Ted Oyama reported that the extra P was necessary[46] though Cho et al. reported no extra P enhances activity of Ni_2P [47]. The extra P seems to compensate the P loss during the reduction and the important thing is to keep the Ni_2P structure. Fine regulation of the P composition and structure in the catalysts are thus necessary to enhance the surface activity. Pure Ni will not act as a HDS catalyst, since the very strong bonding between Ni and S adatoms rapidly poisons the surface active sites. The presence of P enables Ni_2P to serve as a catalyst for the HDS reaction[15], since P dilutes the active Ni sites to reduce the extent of sulfur poisoning, acts to regulate the Ni electronic structure and works to stabilize the Ni_2P surface structure.

In Ni_2P , the surface Ni and P atoms are slightly polarized, such that the Ni and P possess a small amount of positive and negative charge, respectively [35]. Previous investigations have revealed that the surface P/Ni composition seems to be variable, and an Auger electron spectroscopy study has shown that sputtering reduces the P concentration while annealing recovers the stoichiometry composition by promoting bulk diffusion [35].

The P atoms are preferably segregated on the surface in order to stabilize the surface by removing the dangling Ni bond appearing at the Fermi level, as seen in the $\text{Ni}_2\text{P}(10\bar{1}0)-c(2\times 4)$ reconstructed structure and evidenced by the presence of $\text{Ni}_3\text{P}-\text{P}$ on

the Ni₂P (0001)-(1×1) surface. DFT calculations also suggest an approximately -0.5 eV downward shift of the Ni d band to the band between -1.5 eV and -4.5 eV, as well as a peak at -3.9 eV caused by interaction with the topmost P [36].

Although the P atoms can serve as stable adsorption sites for atomic hydrogen [15,36], surface P may also reduce the catalytic activity since P sites do not have the same ability to promote the dissociative adsorption of molecules as the Ni sites [36]. 3-fold Ni hollow sites are active in adsorbing S, H and OH species for different reactions[15]. Atomic hydrogen adsorbs stronger on 3-fold Ni hollow sites than the topmost P sites of the Ni₃P-P surface [36]. The removal of the P might be necessary from the 3 fold Ni site to activate the Ni₂P surface but too many removal of P would reduce the stability of Ni₂P structure. Further studies are necessary to find the appropriate surface composition as well as to reveal the active Ni site.

5. Conclusion

This review covers the surface structures and electronic states of (1×1) and reconstructed Ni₂P (0001) and (10 $\bar{1}$ 0). Both the Ni₂P(0001) and (10 $\bar{1}$ 0) surface structures have been extensively investigated by LEED, STM, XPS, PES and other techniques. The electronic structures of the two orientations have been found to be similar to one another, a main Ni 3d-P 3p band and a satellite band being observed on both surfaces, except for a small peak at 0.6 eV introduced by the surface state of P 3p. (1×1), (2/3×2/3) and ($\sqrt{3} \times \sqrt{3}$)R30° structures are reported for the (0001) plane, while (1×1) and c(2×4) reconstructed structures have been observed in the case of the (10 $\bar{1}$ 0) plane. Since Ni₂P single crystals have exhibited these reconstructed structures, the bulk terminated structure may not be stable. P atoms have been determined to stabilize the Ni₂P surface structure and thus the concentration of surface P is a key factor in controlling the surface activity.

Figure Captions:

Table 1. Adsorption sites for each reaction on Ni₂P(0001) surface.

Figure 1. a) The crystal structure of Ni₂P. b) The Ni(1) site. c) The Ni(2) site. d) An Ni₃P layer composed of Ni(2) and P(1). e) An Ni₃P₂ layer composed of Ni(1) and P (2). Legend: pale pink and dark grey indicate P and Ni, respectively.

Figure 2. The 0th and 1st layer structures of four proposed models of Ni₂P(0001)-(1×1): a) Ni₃P-P, b) Ni₃P-Ni, c) Ni₃P₂-Ni and d) Ni₃P₂-P. The 0th layer atoms are drawn in a darker color [29].

Figure 3. a) Side view of the optimized structure of Ni₃P-P. b) Top view of the 0th and 1st layers of Ni₃P-P. The arrows show the displacement of atoms compared to the bulk material [29].

Figure 4. Side (upper image) and top views (lower image) of a Ni₂P(10 $\bar{1}$ 0) surface based on a (1×1) structure, a MRARM model of a reconstructed Ni₂P(10 $\bar{1}$ 0)-c(2×4) structure [28] and a c(2×2) structure [45]. The topmost visible P atoms are drawn in a darker color. The zigzag line indicates the visible P atoms of the c(2×4) structure.

Figure 5. STM image of a Ni₂P(10 $\bar{1}$ 0) surface containing both c(2×4) and c(2×2) structures: a) a 100 × 100 nm region, b) a zoomed-in image of a c(2×4) structure and c) a zoomed-in image of a c(2×2) structure. V_{bias} = -1.5 V, I_t = 300 pA. (Reproduced from Fig.4 of ref.[45] with permission of Surface Science Society of Japan.)

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