Atomic Structure and Catalytic Activity of W-Modified Ni$_2$P Surface Alloy by Photoelectron Diffraction and Spectroscopy

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I. INTRODUCTION

Removal of the sulfide and nitride contents in natural petroleum feedstock is an urgent issue in the refining industry. The surface properties of transitional metal phosphides (TMPs) have attracted much attention as a new catalyst group for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions [1]. Among the TMPs catalyst group for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions [1]. The surface alloying is the important topics in Ni$_2$P study which is expected for next generation hydrodesulfurization and hydrodenitrogenation catalyst. The atomic structure and catalytic properties of a single crystalline Ni$_2$P surface modified with W (W-Ni$_2$P) was investigated by photoelectron diffraction (PED) and spectroscopy. PED is an element and site selective surface structure analysis method that enables observation of three-dimensional atomic configurations of the surface local structure. The selective replacement of W to the Ni site in the Ni$_2$P crystal was clarified by PED. Chemical reactivities for NO molecules of the W-Ni$_2$P and the clean Ni$_2$P surfaces were compared. On the clean Ni$_2$P surface, the NO adsorption did not occur, whereas W-Ni$_2$P surface showed remarkable activity for NO adsorption. [DOI: 10.1380/ejssnt.2014.53]

Keywords: Photoelectron diffraction measurement; Soft X-ray photoelectron spectroscopy; Catalysis; Surface chemical reaction; Surface alloy; Ni$_2$P; Tungsten; Hydrodenitrogenation

II. EXPERIMENTAL

A single crystalline Ni$_2$P(10T0) surface was used as the substrate [10]. This surface has a stoichiometric composition of Ni$_7$/P=2 which is same as that of bulk, and was suitable for studying the bulk chemical property. The sample size was 5×10×1 mm$^3$. We made an atomically clean surface following the method reported in the previous study [4]. The surface was mechanically polished to a mirror finish and was cleaned by Ar$^+$ sputtering at 2.5 keV (current: 1 μA, time: 30 min, Ar pressure: 1×10$^{-3}$ Pa) and annealing at 350°C by direct current injection repeatedly after transferring into an ultra-high vacuum below 3×10$^{-8}$ Pa. The annealing temperature was monitored by a K-type thermocouple. The surface structure was determined by reflection high-energy electron diffraction (RHEED). A sharp (1×1) structure coming from the clean surface was confirmed. The chemical composition of the sample surface was observed by XPS.

The W-Ni$_2$P surface was prepared by depositing W on a clean Ni$_2$P surface under H$_2$ atmosphere with a pressure of 3×10$^{-3}$ Pa. W filament with φ=0.2 mm and a length
of 200 mm was set less than 10 mm above the sample and was heated at around 2000°C by direct current injection for 10 min. The W-Ni$_2$P surface kept the sharp (1×1) RHEED pattern, indicating that W-modified layers were epitaxially formed on the Ni$_2$P surface. 1000 Langmuir (3×10$^{-3}$ Pa, 100 sec) NO molecules (purity: 99.9%) were dosed at room temperature to compare the chemical reactivity between the W-Ni$_2$P and the clean Ni$_2$P surfaces. The NO adsorbate coverage on the surface was evaluated by XPS.

PIAD from the sample at a specific kinetic energy was most efficiently measured using a two-dimensional display-type spherical mirror analyzer (DIANA) which was installed at the circularly-polarized soft x-ray beamline BL25SU at SPring-8 in Japan [11]. A 2π-stereadian PIAD was obtained by scanning of the sample azimuth and P$_2$ photoelectron intensity angular distributions (PIADs) from the clean Ni$_2$P(10T0) surface, respectively. All PIADs were obtained with the kinetic energy of 600 eV and displayed in azimuth equidistant projection.

FIG. 1: (a) Crystalline structure of Ni$_2$P. Red and yellow spheres indicate Ni and P atoms, respectively. (b) The set of atomic arrangement in Ni$_3$P$_2$ and Ni$_3$P layers. Yellow dotted circles indicate the out plane positions of P atoms. (c) and (d) Set of 2π-stereadian Ni 3p and P 2p photoelectron intensity angular distributions (PIADs) from the clean Ni$_2$P(10T0) surface, respectively. All PIADs were obtained with the kinetic energy of 600 eV and displayed in azimuth equidistant projection.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the crystalline structure of Ni$_2$P. Ni$_2$P belongs to the space group P$_{2\text{mn}}$ of hexagonal symmetry with $a=b=0.586$ nm and $c=0.338$ nm. In the bulk, two kinds of stoichiometric layers, namely Ni$_3$P and Ni$_3$P$_2$ layers, stack alternatively along the [0001] direction. The blue colored rectangle in Fig. 1(a) indicates the {10T0} plane which was used in this study. The {10T0} surface has a mirror symmetric structure with respect to the {0001} plane. Ni has two kinds of atomic sites which are surrounded by tetrahedral and pyramidal P structures in Ni$_3$P$_2$ and Ni$_3$P layers, respectively. Since these tetrahedral and pyramidal Ni sites rotate by 120° in each other, six kinds of photoelectron emitter sites (Ni1-6) are expected as shown in Fig. 1(b). P has three kinds of emitter sites: P1 and P2 sites in Ni$_3$P$_2$ layer and P3 site in Ni$_3$P layer, respectively.

Figures 1(c) and 1(d) show the set of 2π-stereadian Ni 3p and P 2p PIADs from the clean Ni$_2$P(10T0) surface. The different structures appeared in each PIAD owing to the different surrounding atomic configuration for each atomic site. The left and right horizontal directions correspond to the [0001] and [000T], respectively. Mirror symmetric structure with respect to the {0001} plane was observed. A Kikuchi-band-like feature, which originated from the bulk atomic arrangement, was observed along the projection of {0001} plane. Each colored dots along the {0001} plane corresponds to the direction shown in Fig. 1(b). In the P 2p PIAD shown in Fig. 1(d), the additional Kikuchi-band-like features at {1T00} planes appeared. DR, which corresponds to the bond between the P3 atom and the first neighboring Ni5 atom in Ni$_3$P layer, was observed around the [11T0] direction shown with dotted line. The opening angle of DR (44°) corresponded to the inter atomic distance of 0.24 nm.

Figures 2(a), 2(b) and 2(c) are 2π-stereadian Ni 3p, P 2p and W 4f PIADs from the W-modified Ni$_3$P(10T0) surface (W-Ni$_2$P). (d) Signal intensity profiles along the {0001} Kikuchi-band for the element specific PIADs in Figs. 2(a), 2(b) and 2(c).
and after the W deposition. This indicates that the Ni
2p and W 4f dosing.

The signal intensity profiles along the Ni 3p and P 2p positions, diffraction patterns and their circular dichroism
were marked with the sky blue dotted circles in Figs. 2(a),
2(b) and 2(c). Note that these positions are different for
Ni 3p and P 2p, while those of Ni 3p and W 4f coincided.
The signal intensity profile along the [0001] plane for
Figs. 2(a), 2(b) and 2(c) are displayed in Fig. 2(d). The W
and Ni profiles showed similar features, while that of P did
not have intensity around the [01−20] and [10−20] directions.
Thus, the substitution of W to the Ni site in the Ni 3p
plane for the entire crystal was clarified. The destination of substituted Ni
atom is still an open question.

The chemical reactivity difference between W-Ni 3p and
W-Ni 3p surfaces was studied by NO adsorption. This
NO adsorption method is widely used for the study of ac-
tive surface site for HDS catalyst [12]. Figure 3(a) shows
the wide area XPS spectra taken before and after NO
dosing for both surfaces. NO did not adsorb on the clean
surface, while the significant increase of N 1s and O 1s peak intensities were confirmed on the W-Ni 3p
surface. The intensity ratio of O 1s (7.9 counts) versus N
1s (2.9 counts) based on the spectra shown in Fig. 3(a)
was estimated considering crossing section for O 1s (0.18)
and N 1s (0.11) excitations. The intensity of O was 1.7
times as large than that of N, implying that NO gas was
dissociated on the surface and a part of N was desorbed.

Figure 3(b) shows the detailed XPS spectra for W 4f, Ni
3p and P 2p. In the XPS taken before NO dosing, Ni 3p
and P 2p core-level peaks were simple Gaussian disper-
sions, while W 4f had a shoulder structure shifted by 2
eV to higher binding energy due to spin orbit interaction
of 4f7/2 and 4f5/2. After NO dosing, new shoulder struc-
tures appeared in the W 4f and P 2p spectra shifted by 2
and 3.5 eV to higher binding energy, respectively. This
indicates that the dissociated O oxidized W and P, W-Ni 3p
surface showed a possibility of high catalytic properties
which was not observed on the Ni 3p surface.

IV. CONCLUSION

In conclusion, we have characterized the clean and W-
modified Ni 3p(10T0) surfaces by PED. Element specific
PIADs clarified the replacement of W onto the Ni site,
while maintaining the Ni 3p structure. Newly observed W-
Ni 3p on the Ni 3p substrate showed a remarkable activity
for NO adsorption which was not observed on the clean
Ni 3p surface. Therefore, this surface is expected to have
a new catalytic properties. PED combined with XPS was
an useful analysis tool for clarifying the complex alloyed
structure and the catalytic properties.

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