Highly Loaded and Dispersed Ni$_2$P/Al$_2$O$_3$ Catalyst with High Selectivity for Hydrogenation of Acetophenone

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Abstract: Highly loaded and dispersed Ni$_2$P/Al$_2$O$_3$ catalyst was prepared by the phosphidation of Ni/Al$_2$O$_3$ catalyst with Ni loading of 80 wt.% in liquid phase and compared with the Ni/Al$_2$O$_3$ catalyst for the hydrogenation of acetophenone. X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) etc. were used to characterize the textural and structural properties of the prepared catalysts. It was found that the Ni/Al$_2$O$_3$ and Ni$_2$P/Al$_2$O$_3$ catalyst possessed high surface area, loading and dispersion. The Ni/Al$_2$O$_3$ catalyst had higher apparent activity while the Ni$_2$P/Al$_2$O$_3$ catalyst had higher intrinsic activity for the hydrogenation of acetophenone (AP). Remarkably, the Ni$_2$P/Al$_2$O$_3$ catalyst exhibited high selectivity to 1-phenylethanol, due to repulsion of the phosphorous (P$^{δ−}$) for phenyl group and attraction of the nickel (Ni$^{δ+}$) for oxygen atom of carbonyl group, leading to preferential hydrogenation of carbonyl group in acetophenone. The effect of the particle size of the catalyst on the chemical selectivity might be another reason for high selectivity on the Ni$_2$P/Al$_2$O$_3$ catalyst.

Keywords: supported Ni$_2$P catalyst; supported Ni catalyst; hydrogenation; acetophenone; 1-phenylethanol

1. Introduction

1-phenylethanol (PHE), is a significant chemical intermediate and frequently used in the food, pharmaceutical, cosmetic and polymer industries [1], which can be obtained by the selective hydrogenation of acetophenone (AP) on supported metal catalysts. The hydrogenation of AP is usually performed on noble metal catalysts such as Ru [2,3], Pd [4,5], Pt [6,7], and so on. The hydrogenation of AP on Pt and Ru catalysts exhibits high selectivity for the hydrogenation of aromatic ring and poor selectivity for PHE [3,6]. Though supported Ru catalysts had high selectivity for the hydrogenation of carbonyl group of AP to form PHE, it is also active for consecutively converting PHE to ethylbenzene (EB), due to hydrogenolysis [5]. The non-noble metal catalysts, such as Cu [8,9], Co [10,11] and Ni [12–14], are also investigated for the hydrogenation of AP. Among them, the Ni-based catalysts are the most widely used for the hydrogenation of AP. The main product on the Ni-based catalysts is PHE, but variable quantities of byproducts such as cyclohexylmethylketone (CHMK), 1-cyclohexylethanol (CHE) and EB are found with increase of reaction temperature [13,14].

Very recently, Costa and his co-authors found that the hydrogenation of AP on the SiO$_2$ supported Ni$_2$P/Ni$_{12}$P$_3$ catalysts exhibited high selectivity to PHE [15]. Unfortunately, single-phase Ni$_2$P or Ni$_{12}$P$_5$ catalyst was not investigated for the hydrogenation of AP. In addition, the supported Ni$_2$P/Ni$_{12}$P$_3$ catalysts were prepared by wetness impregnation method using the nickel organometallic salts as precursor. This method is difficult for preparing the catalyst containing metal content.
higher than 50 wt.%, due to the solubility of the precursor. Using thermal decomposition of nickel organometallic salts to prepare metal phosphides, the coordination agents remain in the catalysts and must be washed by the large amount of solvent, resulting in the burdens of post-treatment.

Previously, we have successfully prepared supported Ni\textsubscript{2}P catalysts with high loading and dispersion by liquid phase phosphidation of supported Ni catalysts \cite{16,17}. In this work, the Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst was prepared using the same method by phosphidation of Ni/Al\textsubscript{2}O\textsubscript{3} catalyst. The hydrogenation of AP on the Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} and Ni/Al\textsubscript{2}O\textsubscript{3} catalyst was investigated and it was found that the Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst exhibited higher intrinsic activity and selectivity to PHE than the Ni/Al\textsubscript{2}O\textsubscript{3} catalyst.

2. Results and Discussion

2.1. Textural and Structural Properties of the Fresh Catalysts

X-ray diffraction (XRD) patterns of the Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst are shown in Figure 1. For the pattern of Ni/Al\textsubscript{2}O\textsubscript{3} catalyst, the peaks at 44.5°, 51.9° and 76.4° were indexed to (111), (200) and (220) planes of metallic nickel (PDF\#65-0380), respectively. The average crystallite size of metallic Ni in the Ni/Al\textsubscript{2}O\textsubscript{3} catalyst was estimated to be about 4.2 nm (Table 1), according to the Scherrer equation and the (111) diffraction peak at 44.5°. No distinct reflection peaks of Al\textsubscript{2}O\textsubscript{3} were found. For the pattern of Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst, the peaks at 44.5°, 44.6°, 47.4° and 54.2° were indexed to (111), (201), (210) and (300) planes of Ni\textsubscript{2}P (PDF\#65-1989), respectively. The average crystallite size of Ni\textsubscript{2}P was estimated to be about 6.8 nm (Table 1) by the Scherrer equation and the (111) diffraction peak at 40.7°.

![Figure 1. X-ray diffraction (XRD) patterns of the Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst.](image)

Table 1. Textural and structural properties of the Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}/g)</th>
<th>Pore Volume (cm\textsuperscript{3}/g)</th>
<th>Pore Size (nm)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Al\textsubscript{2}O\textsubscript{3}</td>
<td>258</td>
<td>1.69</td>
<td>20.5</td>
<td>4.2</td>
</tr>
<tr>
<td>Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3}</td>
<td>145</td>
<td>0.70</td>
<td>15.6</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Figure 2 shows the transmission electron microscope (TEM) images of Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst. The two catalysts showed fairly uniform nanoparticles, indicating that metallic Ni and Ni\textsubscript{2}P particles on the Al\textsubscript{2}O\textsubscript{3} support were highly dispersed, although the loading of Ni was high to 80 wt.%
in the Ni/Al₂O₃ catalyst. The average particle sizes of Ni and Ni₂P in the two catalysts were 5.8 and 8.2 nm (Table 1), respectively, larger than those calculated by the Scherrer equation, probably due to the presence of other nickel species.

Table 1 also gives the information of the Brunauer-Emmett-Teller (BET) surface areas, pore volumes and pore sizes for the Ni/Al₂O₃ and Ni₂P/Al₂O₃ catalyst. The surface area, pore volume
and pore size of the Ni₃P/Al₂O₃ catalyst considerably decreased, compared with those of the Ni/Al₂O₃ catalyst. This might be due to that the volume expansion for the conversion of Ni to Ni₂P further blocked cross section of the initial pores.

2.2. Surface Properties of the Fresh Catalysts

The surface composition, information on the valence states and chemical environment of Ni and P were obtained by the X-ray photoelectron spectroscopy (XPS) technology. Figure 3 shows the XPS spectra in the Ni 2p region for the Ni/Al₂O₃ and Ni₃P/Al₂O₃ catalyst and P 2p region for Ni₃P/Al₂O₃ catalyst. The Ni 2p region (Figure 3a) of the Ni/Al₂O₃ catalyst exhibited a signal centered at 856.4 eV. The peak can be assigned to Ni²⁺ of the unreduced NiAl₂O₄ and NiO formed during the passivation [18]. The peak centered at 852.4 eV can be assigned to reduced Ni⁰. A broad peak at 861.4 eV was ascribed to strong shake-up process for the Ni 2p₃/₂ signal of Ni²⁺. For the Ni₃P/Al₂O₃ catalyst, Ni 2p core level spectrum contained two signals. The first one is assigned to Niδ⁺ in the Ni₃P phase at 853.1 eV, consisted with that reported at 852.7–853.4 eV [19]. The second one of 856.4 eV was associated with Ni²⁺ of the unreduced nickel aluminate and nickel phosphates during a superficial passivation.

![Figure 3](image-url)

**Figure 3.** X-ray photoelectron spectroscopy (XPS) spectra of the Ni 2p (a) region for the Ni/Al₂O₃ and Ni₃P/Al₂O₃ catalyst and P 2p (b) for the Ni₃P/Al₂O₃ catalyst.

The P 2p region for the Ni₃P/Al₂O₃ catalyst is shown in Figure 3b. The peak at 133.3 eV was contributed to P⁵⁺ of phosphate species formed by the superficial oxidation of Ni₂P during the
passivation. Another peak at 129.4 eV was assigned to reduced P\textsuperscript{5−} in Ni\textsubscript{2}P, consistent with that reported to be 129.5 eV for P\textsuperscript{5−} in metal phosphides \cite{20}. The P (2p\textsubscript{3}/2) binding energy (129.4 eV) was lower than that reported for elemental P (130.2 eV). Simultaneously, the Ni (2p\textsubscript{3}/2) binding energy (853.1 eV) was higher than that reported for Ni\textsuperscript{0} (852.4 eV) and lower than that reported for Ni\textsuperscript{2+} (853.5–854.1 eV) \cite{19}. These indicated that the electron density was transferred from Ni to P, and thus the phosphorous had a partial negative charge (P\textsuperscript{δ−}) and the nickel had a partial positive charge (Ni\textsuperscript{δ+}).

Table 2 gives the P/Ni atom ratios from XPS and an inductively coupled plasma atomic emission spectrometer (ICP) analyses. The surface P/Ni atom ratio calculated by XPS analyses was 0.63, almost same as that (0.62) calculated by ICP analyses. This suggested that surplus phosphorous oxides were not formed in the Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst prepared by triphenylphosphine (PPh\textsubscript{3}) phosphidation in liquid phase. Frequently, phosphorous oxides exist largely on the surface of supported Ni\textsubscript{2}P catalyst prepared by the temperature programmed reduction method (TPR) and block access to adsorption sites of Ni\textsubscript{2}P \cite{21,22}. Thus, the Ni\textsubscript{2}P catalyst using the TPR method possessed low density of active site. Remarkably, the P/Ni atom ratio in the Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst by PPh\textsubscript{3} phosphidation was slightly higher than the Ni\textsubscript{2}P stoichiometric ratio (0.5), probably due to the presence of other nickel phosphides with P/Ni stoichiometric ratio >0.5, such as, Ni\textsubscript{5}P\textsubscript{4} or NiP\textsubscript{2} \cite{16}. Table 2 also gives the bulk composition of the Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst. The loading of Ni in Ni/Al\textsubscript{2}O\textsubscript{3} catalyst was 77.9%, similar to the value desired. After phosphidation, the contents of Ni and P in the Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst were determined to be 60.5% and 19.8%, respectively, also similar to values desired.

Table 2. Chemical composition for the Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni (wt.%)</th>
<th>P (wt.%)</th>
<th>Al\textsubscript{2}O\textsubscript{3} (wt.%)</th>
<th>P/Ni (atom)</th>
<th>Uptake (µmol/g\textsubscript{cat})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Al\textsubscript{2}O\textsubscript{3}</td>
<td>77.9</td>
<td>-</td>
<td>22.1</td>
<td>-</td>
<td>979</td>
</tr>
<tr>
<td>Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3}</td>
<td>60.5</td>
<td>19.8</td>
<td>19.7</td>
<td>0.62</td>
<td>0.63</td>
</tr>
</tbody>
</table>

2.3. The Properties of the Used Catalysts

Figure 4 gives the XRD patterns of the Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst after the hydrogenation of AP. The results showed that metal Ni phase and Ni\textsubscript{2}P phase were the only phase in the used Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst, respectively. According to the Scherrer equation, the average crystallite size of metallic Ni and Ni\textsubscript{2}P were calculated to be 4.4 and 6.7 nm, respectively. The crystallite size of the Ni and Ni\textsubscript{2}P in the used catalysts was almost not changed, compared with that in fresh ones, indicating that metal Ni and Ni\textsubscript{2}P had high stability during the hydrogenation reaction.

Figure 4. XRD patterns of the used Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst.
TEM images of the used Ni/Al$_2$O$_3$ and Ni$_2$P/Al$_2$O$_3$ catalyst are shown in Figure 5. The metal Ni and Ni$_2$P particles were still highly dispersed in the used Ni/Al$_2$O$_3$ (Figure 5a) and Ni$_2$P/Al$_2$O$_3$ (Figure 5b) catalyst. The average particle sizes of Ni and Ni$_2$P were estimated to be 6.0 and 8.0 nm, respectively. Compared with the average particle sizes of Ni (5.8 nm) and Ni$_2$P (8.2 nm) in the fresh ones, the particle sizes in the used catalyst were almost not changed. These also indicated that metal Ni and Ni$_2$P had high stability during the hydrogenation reaction.

![Figure 5a](image1.png)

![Figure 5b](image2.png)

**Figure 5.** TEM images of the used Ni/Al$_2$O$_3$ (a) and Ni$_2$P/Al$_2$O$_3$ (b) catalyst.
2.4. Catalytic Results

The carbonyl group and aromatic ring of AP can be hydrogenated, and the possible reaction pathways are shown in Figure 6. PHE and CHMK can be obtained through hydrogenation of carbonyl group and aromatic ring, and then further hydrogenated to obtain CHE and EB, respectively.

![Figure 6. Reaction network of AP hydrogenation on the metal catalysts.](image)

Figure 7 gives the activities and selectivities for hydrogenation of AP at different reaction temperatures on the Ni/Al₂O₃ and Ni₂P/Al₂O₃ catalyst. Figure 7a shows that the conversion of AP increased with the increase of reaction temperature. At 453 K, the conversion of AP reached 100% on both catalysts. At 373 K, the conversions of AP were 77.9% and 41.0% on the Ni/Al₂O₃ and Ni₂P/Al₂O₃ catalyst, respectively, indicating that the apparent activity for hydrogenation of AP on the Ni/Al₂O₃ catalyst was higher than that on the Ni₂P/Al₂O₃ catalyst.

Figure 7b gives the results of selectivity to PHE on the Ni/Al₂O₃ and Ni₂P/Al₂O₃ catalyst. The main products were PHE and CHE on the Ni/Al₂O₃ catalyst. Minor quantities of CHMK and EB were found in the hydrogenation products. The total selectivity to CHMK and EB (not shown) was less than 5%, even though the reaction temperature reached 453 K. At the same temperature, the selectivity to PHE on the Ni/Al₂O₃ catalyst was 12%. However, the hydrogenation products on the Ni₂P/Al₂O₃ catalyst were PHE and CHE, and no CHMK and EB were observed. The selectivity to PHE was 100% at the reaction temperature from 333 K to 373 K. The selectivity of PHE (95.6%) on the Ni₂P/Al₂O₃ was significantly higher than that (12%) on the Ni/Al₂O₃ at 453 K.

To compare the intrinsic activities of Ni/Al₂O₃ and Ni₂P/Al₂O₃ catalyst, the effect of weight hourly space velocity (WHSV) on the hydrogenation of AP at 433 K was performed and shown in Figure 8a. It was found that the conversion of AP on the two catalysts decreased with the increase of WHSV of AP.

The density of active site on surface of Ni and Ni₂P catalysts is generally evaluated by the H₂ and CO uptake, respectively [16,23,24]. The H₂ and CO uptake on the Ni/Al₂O₃ and Ni₂P/Al₂O₃ was determined to be 979 and 338 µmol/gcat. (see Table 2), respectively. According to uptakes of chemical adsorption, turnover frequencies (TOF) of AP on the two catalysts can be calculated. The results are shown in Figure 8b. The TOF of AP increased with increase of WHSV and almost reached constant values of about 0.006 and 0.025 s⁻¹ at a WHSV of 8 h⁻¹ on the Ni/Al₂O₃ and Ni₂P/Al₂O₃, respectively. Apparently, the intrinsic activity of Ni₂P/Al₂O₃ catalyst was much higher than that of Ni/Al₂O₃ catalyst.
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Figure 8c shows the selectivity to PHE against WHSV of AP. The selectivity to PHE on the Ni/Al₂O₃ and Ni₂P/Al₂O₃ catalyst was almost not changed with the increase of WHSV and maintained at about 31% and 98%, respectively. The selectivity to PHE on the Ni₂P/Al₂O₃ was significantly higher than that on the Ni/Al₂O₃, consistent with that reported by Dolly and his co-authors for hydrogenation of AP on the supported nickel phosphides [15]. The results might be caused by the following two reasons. The first one was attributed to the special structure of the active sites on Ni₂P surface. The bond length of Ni-P in Ni₂P and C-C between aromatic ring and carbon atom of the carbonyl group is 0.22 nm and 0.15 nm [25], respectively. This demonstrates that the position of P might be matched with the center of the aromatic ring. From XPS results, it is known that the phosphorous had a partial negative charge (P⁻) in Ni₂P, which repulsed the phenyl group away the surface of catalyst. Simultaneously, the nickel had a partial positive charge (Ni⁸⁺) in Ni₂P, attracting the oxygen atom of carbonyl group to the surface of catalyst. These lead to preferential hydrogenation of carbonyl group. Another reason might be attributed to the effect of supported metal particle size. The selectivity of the hydrogenation reaction is significantly affected by the metal particle size of the catalyst, due to the different adsorption configurations of reactant molecules on the catalysts with different particle size. There are two configurations for the adsorption of AP on the metal catalyst. For the first configuration, the oxygen atoms are linearly absorbed on the surface Ni sites and the carbonyl groups are parallel to the catalyst surface, leading to simultaneous hydrogenation of carbonyl...
group and aromatic ring. For the second configuration, the carbonyl groups are adsorbed through the π electrons (bridged adsorption) on the surface Ni sites and the aromatic rings are tilted to the catalyst surface, leading to preferential hydrogenation of carbonyl group [7]. The carbonyl group is mainly absorbed on the catalyst with large metal particle size through the bridged adsorption while on the catalyst with small metal particle size through the linear adsorption [26]. The Ni$_2$P particle size (8.2 nm) is larger than the Ni particle size (5.8 nm). AP absorption on Ni$_2$P catalyst had more bridged configuration. Thus, the Ni$_2$P/Al$_2$O$_3$ exhibited higher selectivity to PHE than the Ni/Al$_2$O$_3$.

![Figure 8](image_url)

**Figure 8.** Conversions (a), turnover frequencies (TOF) (b) of AP and selectivity to PHE (c) vs. WHSV of AP over the Ni/Al$_2$O$_3$ and Ni$_2$P/Al$_2$O$_3$ catalyst. Reaction conditions: $p = 3.0$ MPa, $H_2$/AP = 5, $T = 433$ K.
3. Materials and Methods

3.1. Catalyst Preparation

The precursor of Ni/Al\textsubscript{2}O\textsubscript{3} catalyst with Ni loading of 80 wt.% was prepared by improved co-precipitation method. Briefly, the desired quantities nickel nitrate and aluminum nitrate were dissolved in an aqueous solution of deionized water. The desired amount of sodium carbonate was dissolved in another aqueous solution of deionized water. The above two solutions were simultaneously added into a vessel with 200 mL deionized water at 353 K under continuous stirring. The green precipitates were washed in deionized water six times. The washed precipitates were re-dispersed in 200 mL n-butanol and evaporated at 353 K. Then sample was further dried in electric oven at 393 K to obtain the precursor of Ni/Al\textsubscript{2}O\textsubscript{3} catalyst. The precursor was reduced in H\textsubscript{2} (0.1 MPa and 40 mL/min) at 723 K for 2 h and cooled down to a reaction temperature, at which the feeding was fed into the reactor and the hydrogenation of AP began in situ.

The Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst was prepared by the phosphidation with triphenylphosphine (PPh\textsubscript{3}) in liquid phase. The same phosphidation procedure was described previously [16]. Briefly, the Ni/Al\textsubscript{2}O\textsubscript{3} catalyst was loaded into a reactor and reduced in H\textsubscript{2} (0.1 MPa and 40 mL/min) at 723 K for 2 h to form Ni/Al\textsubscript{2}O\textsubscript{3} catalyst. Then, the temperature was cooled down to 443 K and the Ni/Al\textsubscript{2}O\textsubscript{3} was phosphided with PPh\textsubscript{3} (2%) in heptane solution (Liquid hourly space velocity (LHSV) of 2 h\textsuperscript{-1} and H\textsubscript{2}/oil of 300 v/v) for 36 h. Afterwards, the sample was treated in H\textsubscript{2} at 673 K for 3 h to form Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst. The catalyst was then cooled down to a reaction temperature, at which the feeding was fed into the reactor and the hydrogenation of AP began in situ.

3.2. Catalyst Characterization

The Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst were prepared separately for characterizations. The preparation was same as those described above. The prepared catalysts were passivated at room temperature under 0.5 vol.% O\textsubscript{2} in N\textsubscript{2} for 12 h and then characterized by different techniques.

TEM was obtained on a JEM-2100 (JEOL, Tokyo, Japan) high-resolution microscope operating at 200 kV. The samples were dispersed in 5% ethanol solution and dropped onto a copper grid coated with a carbon film.

XRD patterns were recorded on a D8 Advance powder diffractometer (Bruker Biosciences Corporation, Billerica, MA, USA) using a Cu K\textalpha source (\(\lambda = 0.1541 \text{ nm}\)) at 40 KV and 40 mA. The 2\texttheta scans covered the range of 20 to 80\degree with a step of 0.02\degree.

The specific surface areas (S\textsubscript{BET}), pore volume and pore size were measured at 77.3 K using a Micromeritics Gemini V 2380 autosorption analyzer (Micromeritics Corporation, Norcross, GA, USA).

XPS measurements were carried out by a Thermo ESCALAB 250 (Thermo Fisher Scientific, Waltham, MA, USA) with Al K\textalpha (1486.6 eV) line at 150 W.

The chemical compositions of the catalysts were obtained using an inductively coupled plasma atomic emission spectrometer (ICP-AES, ICPS-7510, Shimadzu Corporation, Tokyo, Japan).

H\textsubscript{2} and CO chemisorption isotherms at 308 K were performed to measure H\textsubscript{2} and CO uptake of Ni/Al\textsubscript{2}O\textsubscript{3} and Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3}, respectively. The precursor of Ni/Al\textsubscript{2}O\textsubscript{3} catalyst was reduced in H\textsubscript{2} at 723 K for 2 h while the passivated Ni\textsubscript{2}P/Al\textsubscript{2}O\textsubscript{3} catalyst was re-reduced in H\textsubscript{2} at 673 K for 3 h and then evacuated at the corresponding reduction temperature for 1 h. After cooling to 308 K, the chemisorption of H\textsubscript{2} or CO was performed. The uptakes of H\textsubscript{2} and CO were estimated by extrapolating the linear portion of the isotherm to \(p = 0\).

3.3. Catalytic Tests

The hydrogenation of AP was carried out at 3.0 MPa pressure in a continuous flow fixed-bed microreactor (inner diameter 10 mm). The catalyst sample of 1.0 g (40–60 mesh) was mixed with quartz sand. The feeding consisted of a solution of 33.3 wt.% AP in ethanol and the H\textsubscript{2}/AP was 5 (molar ratio). The products were analyzed by a gas chromatograph equipped with a flame ionization
detector (FID) and a HP-FFAP capillary column. The TOF was calculated by dividing the number of molecules converted per second by the number of active nickel atoms on the surface measured by $H_2$ (for Ni/Al$_2$O$_3$) or CO (for Ni$_2$P/Al$_2$O$_3$) adsorption.

4. Conclusions

A highly dispersed and loaded Ni/Al$_2$O$_3$ catalyst was prepared by the co-precipitation and subsequently phosphided by PPh$_3$ in liquid phase to form Ni$_2$P/Al$_2$O$_3$ catalyst, which possessed high dispersion and loading of Ni$_2$P. XPS results showed that the phosphorous had a partial negative charge ($P^{5-}$) and the nickel had a partial positive charge ($Ni^{5+}$) on the surface of Ni$_2$P/Al$_2$O$_3$ catalyst.

The hydrogenation of AP was performed on the Ni/Al$_2$O$_3$ and Ni$_2$P/Al$_2$O$_3$ catalyst. The results showed that the Ni/Al$_2$O$_3$ catalyst had higher apparent activity than the Ni$_2$P/Al$_2$O$_3$ catalyst. However, the Ni$_2$P/Al$_2$O$_3$ catalyst possessed higher intrinsic activity than the Ni/Al$_2$O$_3$ catalyst. In particular, the Ni$_2$P/Al$_2$O$_3$ catalyst exhibited higher selectivity to PHE than the Ni/Al$_2$O$_3$ catalyst. This might be caused by the following two reasons. First, $Ni^{5+}$ in Ni$_2$P attracted the oxygen atom of carbonyl group to the surface of catalyst while $P^{5-}$ in Ni$_2$P repulsed the phenyl group away the surface of catalyst, leading to preferential hydrogenation of carbonyl group in AP. Second, the effect of particle size of Ni$_2$P catalyst might be another reason for high selectivity to PHE.

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