

Short communication

# Small amorphous and crystalline Ni–P particles synthesized in glycol for catalytic hydrogenation of nitrobenzene

Ping Liu<sup>a,\*</sup>, Wan-Ting Chang<sup>a</sup>, Xue-Yuan Liang<sup>a</sup>, Jun Wang<sup>b</sup>, Yong-Xin Li<sup>a,\*</sup><sup>a</sup> Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Institute of Petrochemical Technology, Changzhou University, Changzhou, Jiangsu 213164, China<sup>b</sup> State Key Laboratory of Materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China

## ARTICLE INFO

## Article history:

Received 28 October 2015

Received in revised form 23 December 2015

Accepted 24 December 2015

Available online 28 December 2015

## Keywords:

Amorphous Ni–P

Nickel phosphide

Solvothermal method

Hydrogenation of nitrobenzene

## ABSTRACT

Amorphous and crystalline Ni–P particles were synthesized *via* atmospheric solvothermal method using the cheap materials of nickel chloride hexahydrate and sodium hypophosphite. The Ni–P samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. Uniform and small Ni–P particle sizes were obtained at facile conditions, and the phase state of Ni–P could be controlled conveniently by adjusting the synthetic time. In the hydrogenation of nitrobenzene, the amorphous Ni–P gave much higher activities compared to the counterpart crystalline Ni–P.

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## 1. Introduction

In recent years, amorphous and crystalline Ni–P catalysts attract much attention due to their excellent activity, high selectivity and strong sulfur resistance in many hydrotreating reactions [1–5]. The Ni–P materials are quite promising to be the next generation of hydrogenation catalysts replacing the expensive Pd or Pt.

Significantly, the catalytic activity of Ni–P is closely related to their particle sizes. Bulk Ni–P has almost no catalytic ability, while small Ni–P particles show higher activities [6,7]. However, during the synthesis process, Ni–P particles are usually susceptible to severe agglomeration because of much high surface energy [8]. In order to enhance the activity of Ni–P, many attempts have been made to increase the density of active sites on the surface of Ni–P catalysts [9–13]. On the one hand, various porous and hollow Ni–P were researched extensively [10,11]. For these synthesized Ni–P catalysts, the specific surface areas were raised with improved catalytic activities. However, complicated experimental steps and expensive template agents were indispensable in these synthesis processes. On the other hand, small Ni–P particles have been controllably synthesized using expensive trioctylphosphine (TOP) or Ni<sub>(11)</sub>acetylacetonate (Ni(acac)<sub>2</sub>) [12,13]. Nevertheless, for the industrial application of Ni–P, it is essential to explore facile, simple and low-cost methods to synthesize Ni–P nanoparticles with high catalytic activity.

In the present work, cheap materials of nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O) and sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>) are employed to synthesize small amorphous and crystalline Ni–P particles in glycol at facile conditions. Their catalytic performances are investigated in the hydrogenation of nitrobenzene.

## 2. Experimental

## 2.1. Catalyst preparation

The Ni–P nanoparticles were synthesized *via* atmospheric solvothermal method with glycol as the solvent. In detail, nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O) and sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>) (Ni/P molar ratio of 1/3) were added into 20 mL glycol in a 50 mL round-bottom flask. Under reflux, the mixture was stirred at 170 °C for a certain time (10 min–15 h). After the system was cooled to room temperature naturally, the dark precipitates were collected by centrifuge, washed with ethanol and deionized water for several times, and then dried in a vacuum at 50 °C for 3 h. The obtained Ni–P nanoparticles were marked as Ni<sub>x</sub>P<sub>s</sub> (*x* stands for the actual molar ratio of Ni/P obtained by XPS analysis).

For comparison, Ni–P sample prepared in a tube furnace was investigated using the same Ni and P sources. NiCl<sub>2</sub>·6H<sub>2</sub>O and NaH<sub>2</sub>PO<sub>2</sub> with a Ni/P molar ratio of 1/3 were dissolved in 10 mL deionized water. After stirring for 0.5 h, the mixture was evaporated to dehydrate, followed by drying at 100 °C over night and treating in N<sub>2</sub> flow at 300 °C for 1 h. The product was then washed with ethanol and deionized water, and dried

\* Corresponding authors.

E-mail addresses: [pingliu02@163.com](mailto:pingliu02@163.com) (P. Liu), [liyxluck@163.com](mailto:liyxluck@163.com) (Y.-X. Li).

in a vacuum at 50 °C for 3 h. Crystalline Ni<sub>2</sub>P-f (marked as Ni<sub>2</sub>P-f) was obtained through the synthesized process.

## 2.2. Characterization

The phase identification was recorded by X-ray diffraction (XRD) with a Bruker D8 Advance X-ray diffractometer using Cu K $\alpha$  radiation, employing a scanning rate of 2°·min<sup>-1</sup> and scanning range of 5–80°. The morphology was specified by scanning electron microscopy (SEM) on a QUANTA 200 (FEI) and transmission electron microscopy (TEM) using a JEOL JEM-2100 high resolution transmission electron microscope. X-ray photoelectron spectroscopy (XPS) was recorded on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg or Al K $\alpha$  radiation.

## 2.3. Catalytic tests

The catalytic performances of the synthesized Ni–P catalysts were tested in the hydrogenation of nitrobenzene. Typically, 20 mg catalyst, 0.5 mL nitrobenzene, and 10 mL ethanol were added into a 50 mL stainless steel autoclave. After replacing the air in the autoclave with argon, 1.0 MPa H<sub>2</sub> was injected, and the catalytic tests were then performed at 100 °C for 1 h. The products were analyzed by GC with a SE-54 capillary column using toluene as the internal standard. The recovered catalyst was washed with ethanol, and then stored in ethanol for the next run.

## 3. Results and discussion

### 3.1. Characterization of catalysts

#### 3.1.1. XRD

As shown in Fig. 1, sharp diffraction peaks at 40.7, 44.6, 47.4, 54.2 and 74.8° were detected for Ni–P catalyst synthesized in the tube furnace, indicating the formation of Ni<sub>2</sub>P hexagonal structure [14]. For various Ni<sub>x</sub>P-s samples prepared by atmospheric solvothermal method in glycol, amorphous and crystalline structures were obtained at different synthetic times. Less than three hours, the products with a broad peak at  $2\theta = 45^\circ$  were mainly amorphous Ni<sub>x</sub>P-s particles. When the synthetic time reached 3 h, a much weak peak at 47.4° was observed. It suggests that the crystalline structure of Ni<sub>x</sub>P-s is beginning to form. More than 5 h, three obvious diffraction peaks at about 32.8, 42.4, and 47.4° (indexed as the Ni<sub>12</sub>P<sub>5</sub> phase [15,16]) were detected, verifying

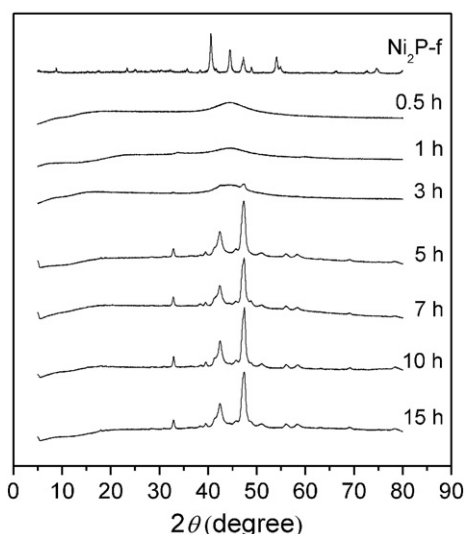


Fig. 1. XRD patterns for Ni<sub>2</sub>P-f and Ni<sub>x</sub>P-s samples synthesized at different times.

crystalline nature of Ni<sub>x</sub>P-s. The XRD results show that it is convenient to control the phase state of Ni–P by adjusting the synthetic time.

#### 3.1.2. SEM

Fig. 2 shows the morphologies of Ni<sub>2</sub>P-f and various Ni<sub>x</sub>P-s samples. Large particles of Ni<sub>2</sub>P-f with about 1  $\mu$ m were observed in its TEM image. In comparison, much smaller particles for amorphous and crystalline Ni<sub>x</sub>P-s were obtained. It is owing to the lower synthetic temperature (170 °C) and the stabilizing effect of glycol to Ni<sub>x</sub>P-s nanoparticles. In general, the synthesized Ni<sub>x</sub>P-s was consisted with many lumps. Exceptionally, the Ni<sub>x</sub>P-s sample synthesized at 0.5 h was composed by some particles with petals shape. Among these Ni<sub>x</sub>P-s samples synthesized at different times, amorphous Ni<sub>x</sub>P-s possessed uniform and very small particle sizes of about 80 nm, while crystalline Ni<sub>x</sub>P-s exhibited some agglomeration phenomenon. It indicates that high surface energy exists on the Ni<sub>x</sub>P-s particles, and urges agglomerating of these nanoparticles under their collision. Therefore, more agglomeration appeared with increasing the synthetic time as shown in Fig. 2.

#### 3.1.3. XPS

XPS spectra of Ni and P 2p for Ni<sub>x</sub>P-s samples synthesized at 1 and 5 h are showed in Fig. 3. In Ni 2p spectrum for Ni<sub>x</sub>P-s-1 h, the Ni 2p<sub>3/2</sub> peaks appeared at 855.8 and 852.5 eV are corresponding to the Ni 2p<sub>1/2</sub> peaks at 869.7 and 873.5 eV. The Ni 2p<sub>3/2</sub> peak at 852.5 eV could be assigned to Ni <sup>$\delta$ +</sup> ( $0 < \delta < 2$ ) and the peak at 855.8 eV to Ni<sup>2+</sup> [17]. A broad satellite peak at 860.9 eV was assigned to divalent species or trivalent nickel species in the reported literature [18]. For P 2p spectrum for Ni<sub>x</sub>P-s-1 h, the peaks at 129.3 and 132.9 eV were assigned to P <sup>$\delta$ -</sup> ( $0 < \delta < 1$ ) and P<sup>+</sup> of H<sub>2</sub>PO<sub>2</sub><sup>-</sup> [19], respectively. The existence of Ni<sup>2+</sup>

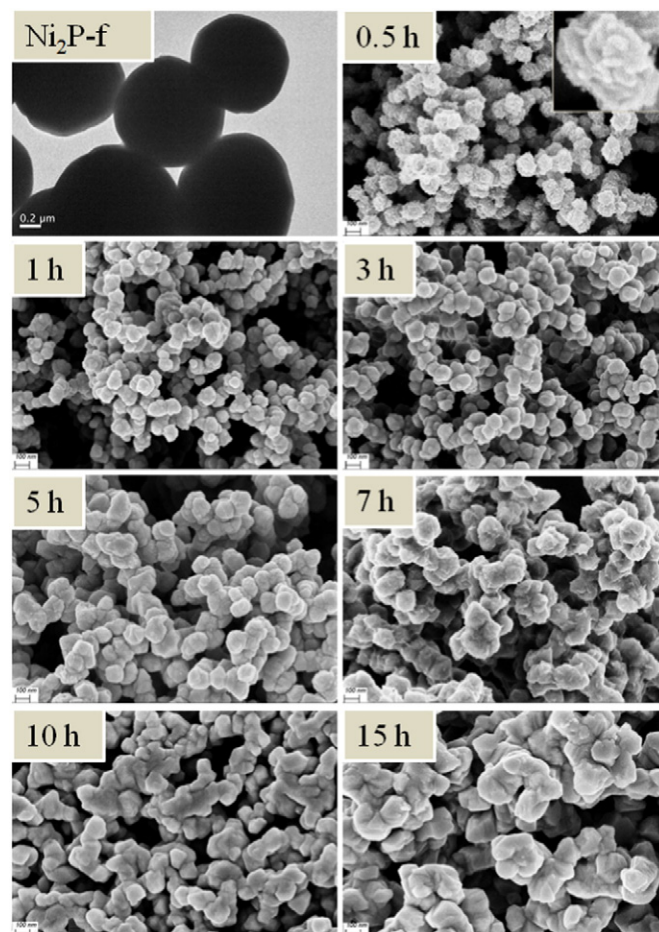


Fig. 2. TEM image of Ni<sub>2</sub>P-f and SEM images of various Ni<sub>x</sub>P-s samples.

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