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Short Communication

New bulk nickel phosphide catalysts for glycerol hydrogenolysis to 1,2-propanediol

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ABSTRACT

Transitional metal phosphides were found to have outstanding activity and stability in catalytic hydrotreatments. The bulk trinickel phosphide catalyst with the smallest phosphorus content among the nickel phosphides were synthesized by a hydrothermal method followed by an annealing treatment, and the resulting bulk trinickel phosphide catalysts presented a high purity and morphology of hexagonal prisms. The optimized synthesis conditions include a P:Ni ratio of 3 to 1 and a pH value of 5 in the hydrothermal synthesis stage and a calcination temperature of 773 K in the annealing treatment. The synthesized trinickel phosphides exhibited a low-temperature activity to selective glycerol hydrogenolysis and the high selectivity to 1,2-propanediol.

1. Introduction

Traditional metal phosphides have attracted considerable attentions in the recent decades due to their excellent properties and wide application scopes [1]. Used as catalysts, metal-rich phosphides exhibit higher catalytic activity than the traditional sulfide catalysts in hydrotreatments and much better stability than other interstitial compounds such as carbides and nitrides [2]. Especially, the metal-rich nickel phosphides like Ni_2P was found to possess the highest catalytic activity among the traditional metal phosphides for the hydrodesulfurization (HDS) reaction of the FCC naphtha [2].

In our previous work, Ni_2P catalysts were synthesized by the solid phase reaction between the nickel cations and hypophosphites at a much lower temperature than that used in phosphide synthesis by the temperature-programmed reduction of nickel phosphates, and the resulting Ni_2P catalysts presented high dispersion degree and thus high catalytic activity in HDS [3,4]. Trinickel phosphide (Ni_3P) is the nickel-rich phosphide with the smallest content of phosphorus and has a tetragonal crystal structure. It is often found as a main component in the nickel-containing electroless coating, which is a mixture of Ni and Ni_3P and prepared by plating without electric current [5]. Supported Ni_3P was also tried as catalysts for the synthesis of carbon nanotubes [6] and the hydrodechlorination of chlorobenzene [7]. Generally, high ratio of nickel to phosphorus in Ni_3P catalysts means more chance for the exposure of metal nickel to the reactants, which might lead to higher catalytic activity than other nickel-rich phosphide catalysts such as Ni_2P and $Ni_{12}P_5$. Ni_3P can be synthesized by chemical reactions in "chemical plating" [8] or by electrochemical deposition [4]. Supported Ni_3P catalysts were synthesized by temperature-programmed reduction of phosphate at a temperature up to 923 K [7].

In the present work, bulk Ni_3P catalysts were synthesized by a hydrothermal method followed by an annealing treatment. The resulting Ni_3P samples were tested as catalysts for selective glycerol hydrogenolysis to 1,2-propanediol, which is thought a fundamental reaction in a conversion from biomass to fuel for vehicle in the background of diminishing fossil resource reserves and increasing environmental concerns [9–16]. To our knowledge, the pure bulk Ni_3P is synthesized and used for glycerol hydrogenolysis to 1,2-propanediol for the first time.

2. Experimental

2.1. Catalyst synthesis

All chemical reagents were of analytical grade and used as received. Bulk trinickel phosphide catalysts were synthesized by a hydrothermal method followed by an annealing treatment at N_2 atmosphere. In a typical synthesis, nickel hypophosphite and ammonium hypophosphite with a P:Ni atomic ratio of 3:1 were dissolved by deionized water, and the pH value of the resulting green solution was adjusted to 5 by an aqueous solution of ammonia (25 wt.%). The solution then was transferred to a 100 mL Teflon-lined stainless steel autoclave. The autoclave was heated to 423 K and maintained at the temperature for 12 h in a drying oven, and then cooled to room temperature naturally. The mixtures obtained by the hydrothermal method were repeatedly washed with deionized water and filtered, and the resulting black intermediates

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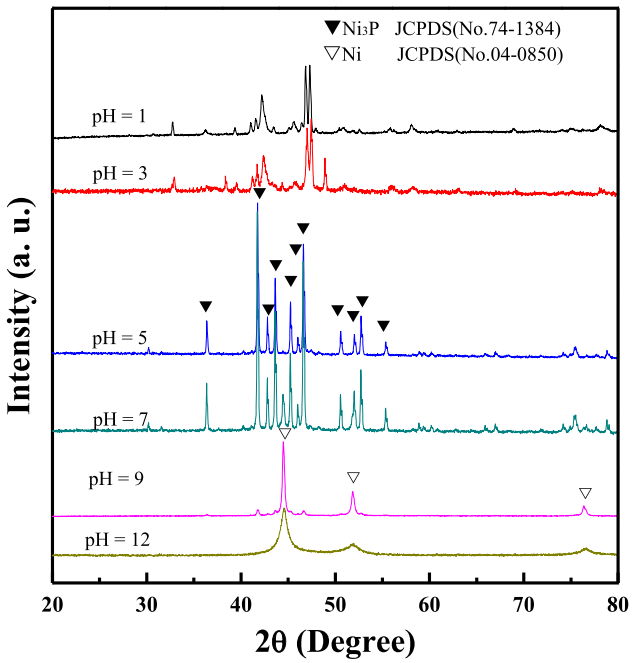

Fig. 1. The XRD patterns of the samples synthesized under different pH values at 423 K for 12 h followed by an annealing treatment at 773 K in a flowing N_2 of 100 sccm for 3 h.

were collected. The annealing treatment of the intermediates was performed in a horizontal furnace with a quartz tube at a temperature of 773 K in a flowing N_2 of 100 standard cubic centimeter per minute (sccm) for 3 h. The annealed products was washed for 3 times by the aqueous solution of ammonia followed by deionized water until the pH value of the filtrate was up to 7. The obtained catalysts were dried at 373 K for 12 h in a static air atmosphere before the evaluation and characterization.

2.2. Catalyst characterization

The Brunauer–Emmett–Teller (BET) surface areas were measured by the Sorptomatic 1990 instrument (Thermo Finnigan). Experiments were performed at 77.3 K using N_2 as the adsorbate. The elemental composition was determined by atomic emission spectroscopy with Perkin Elmer ICP-OES spectrometer. Powder XRD tests were carried out in X-ray diffraction (XRD) patterns and were collected in an ambient atmosphere by a Bruker D8 Advance system using Cu Kα radiation. The 2θ scans covered a range of 10-80° with a step of 0.02°. The applied voltage and current were 40 kV and 40 mA, respectively. Transmission electron microscopy (TEM) analysis was carried out using a Philps Tecnail 12 transmission electron microscope. The samples were prepared by dispersing the powder material in ethanol and dropping the solution on a carbon-coated Cu grid. The hydrogen temperature-programmed desorption (H_2-TPD) of the samples were performed by a chemical adsorption instrument equipped with a thermal conductivity detector (TCD). The samples were pretreated at 373 K in a flowing Ar for 2 h, and then 5% H_2/Ar mixture was introduced through the reactor for H_2-adsorption of the samples for 40 min when the temperature were decreased to 303 K. The H_2-TPD curves were obtained at a ramp of 10 K/min with 50 sccm of Ar from 303 K to 1073 K.

2.3. Catalytic test

The glycerol hydrogenolysis reaction was carried out in a 50 mL Teflon-lined stainless steel autoclave. In a typical test, 30 g of glycerol was dissolved in 27 g of deionized water, and 300 mg of catalyst was then added into the autoclave reactor. The reactor was sealed and repeatedly flushed with hydrogen to eliminate the air, then was heated to 463 K and pressurized to 5.5 MPa by H_2. The product analysis was performed when the reactor was quenched to room temperature by an ex-situ gas chromatograph (SP 6890) equipped with a flame ionization detector (FID) and a capillary column (SE54, 30 m × 0.32 mm).

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples synthesized under different pH values, which then were calcined at 773 K in a flowing N_2 atmosphere for 3 h. It was found that the pH values in the synthesis process of the precursors remarkably affected the phases of the annealed samples. The sample synthesized under a pH value of 9 mainly presented the diffraction peaks of the metallic nickel after annealing, and the sample synthesized at a higher pH value (pH 12) was found to be pure amorphous metallic nickel proved by XRD. The relatively strong diffraction peaks of Ni_3P were observed when the pH value was

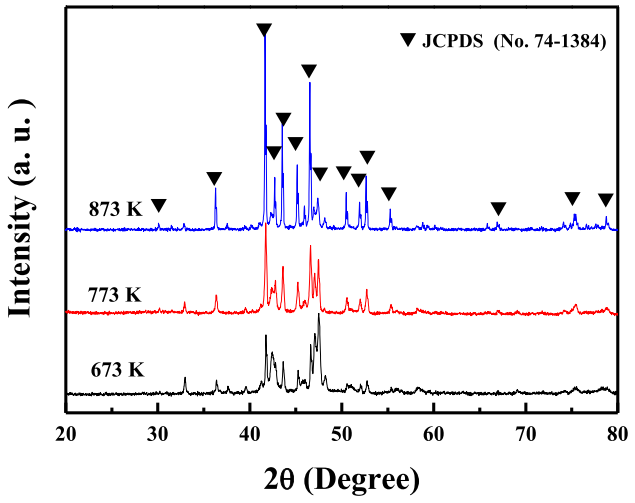

Fig. 2. The XRD patterns of the samples synthesized under a pH value of 5 at 423 K for 12 h followed by an annealing treatment at different temperatures in a flowing N_2 of 100 sccm for 3 h.

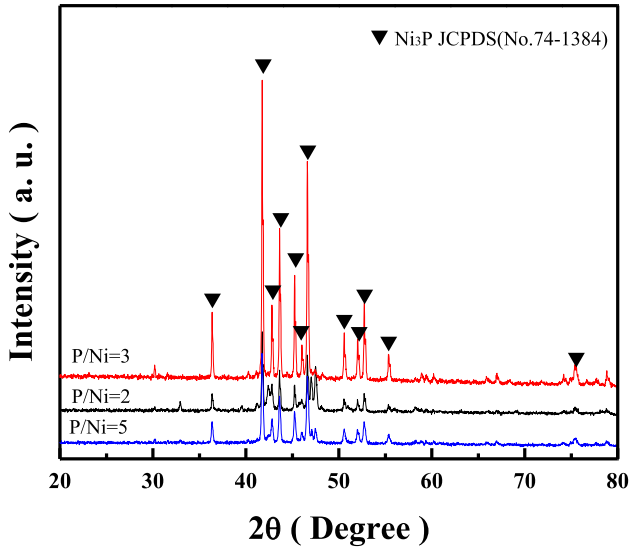

Fig. 3. The XRD patterns of the samples synthesized with different P/Ni ratios under a pH values of 5 at 423 K for 12 h followed by an annealing treatment at 773 K in a flowing N_2 of 100 sccm for 3 h.