Hydrothermal synthesis and photocatalytic degradation ability of nickel phosphide micro/nano materials

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Abstract. Ni$_{12}$P$_5$ and Ni$_2$P catalysts were successfully synthesized by using water as solvent at a low temperature by hydrothermal method. The influence of molar ratio of P/Ni and hydrothermal reaction temperature was studied. The results showed that with initial P/Ni mole increment, pure tetragonal nickel phosphide (Ni$_{12}$P$_5$) could be transformed into pure hexagonal nickel phosphide (Ni$_2$P), while with temperature increment, Ni$_2$P could be gradually transformed into Ni$_{12}$P$_5$. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the phase and morphology of the as-prepared catalysts. The catalysts exhibited better photocatalytic degradation abilities for methylene blue under 365nm ultraviolet irradiation.

1. Introduction

In the past a few years, transitional metal phosphide, in particularly, nickel phosphides have been considered as a new type catalyst in the field of hydroprocessing, hydrogenation of nitro-compounds, adsorption of heavy metals and photocatalytic degradation reaction of organic dyes [1-3]. Besides, Ni$_2$P or CoP exhibited high catalytic activity and stability toward the hydrogen or oxygen evolution reaction [4-7]. Moreover, Ni$_2$P has been an attractive LIB anode material because of its high capacities and low polarization [8]. In numerous of preparation methods of nickel phosphides, hydrothermal synthesis method has many advantages of low cost, mild preparation conditions, non-pollution, morphology and size controlled [2]. Also, stoichiometric ratio of nickel phosphide is very rich, P$^5-$ ion is not stable in water system, so by changing the reaction parameters such as hydrothermal temperature, time, ratio of precursors, solvent or surfactant type, different crystalline phases and morphology of nickel phosphide products can be obtained such as dendric Ni$_3$P [9], hollow spherical Ni$_3$P, Ni$_{12}$P$_5$ [10, 11], unchin-like Ni$_3$P, Ni-P [3, 12], honeycomb Ni$_{12}$P$_5$ [13]. In this paper, Ni$_2$P$_3$ and Ni$_2$P catalysts were successfully synthesized by controlling molar ratio of P/Ni and hydrothermal reaction temperature at a low temperature by hydrothermal method. Furthermore, the photocatalytic degradation of as-prepared catalysts for methylene blue was investigated.

2. Experimental section

2.1. Materials and instruments
Ni(NO$_3$)$_2$·6H$_2$O, (NH$_4$)$_2$H$_2$PO$_4$, red phosphorus, ethanol and methylene blue were purchased from Sinopharm Chemical Reagent Co. Ltd. Photocatalytic device with 250w high pressure mercury lamp was home-made, main emission wavelength of which is 365nm.
2.2. Hydrothermal synthesis of nickel phosphide

Taking molar ratio 4/1 of phosphorus to nickel for example. Take 0.0375 mol of nickel nitrate and 50 ml of distilled water into a 100 ml beaker, fully stirring until the solution is clarified, then add 0.15 mol grinded red phosphorus, put the beaker into a water bath with electromagnetic stirrer for Ostwald ripening 2 h, put the suspension into a 100 mL of high-pressure reaction kettle with teflon as interior material, sealed, followed by drying at 120 °C. After it, the reaction kettle was cooled to room temperature. The obtained black solid material in the kettle was collected and centrifuged to remove impurities with hot distilled water and ethanol in turn, finally vacuum drying for 12 hours under 60 °C. Operation process for different molar ratio of phosphorus to nickel (1/1, 2/1, 6/1, 8/1) is the same as the above.

2.3. Photocatalytic degradation experiment of methylene blue

Add 0.05 g Ni$_2$P$_3$ and Ni$_3$P nanoparticles to 50 ml of 10 mg/L of methylene blue solution, respectively. Adopt magnetic stir for 15 min to make nickel phosphide evenly dispersed in the solution, then put the solution in photocatalytic device under UV illumination, keeping the distance from the lamp to the solution about 20 cm. During photocatalytic degradation, take a sample every 30 minutes followed high speed centrifuge and take out supernatant fluid, then measure absorbance of the solution at 665 nm for different reaction time by T6 ultraviolet-visible spectrophotometer. The procedure of blank test is the same as the above, but only difference is no nickel phosphide catalyst. The degradation rate of methylene blue solution was calculated by $\frac{(A_0-A_1-\Delta A)}{A_0}$, where $A_0$ and $A_1$ is the absorbance of solution before and after photocatalytic experiment, respectively, $\Delta A$ is the absorbance changes of methylene blue solution in blank test.

2.4. Catalysts characterization

The XRD patterns were measured on a Rigaku D/Max 2500X diffractometer using nickel filtered Cu Kα radiation at 40 kV and 80 mA. Transmission electron microscope (TEM) images of catalysts were obtained on a JEM2100 model. The sample was placed on a 200-mesh copper grid coated with carbon.

3. Results and Discussion

3.1. The influence of initial molar ratio of P/Ni

The XRD patterns of as-prepared products (figure 1) shows the effect of the different initial molar ratio of P/Ni on the crystal phase of as-prepared products. The peaks at 20 of 8.1°, 14.0°, 19.9°, 24.4°, 28.2°, 32.8° can be attributed to the characteristic peaks of Ni$_{11}$(HPO$_3$)$_3$(OH)$_6$(PDF44-1327) when initial n(P)/n(Ni) is 1/1or 2/1. When initial n(P)/n(Ni) is 4/1, the characteristic peaks at 20of 32.7°, 35.8°, 38.4°, 41.7°, 44.4°, 47.0°, 49.0° can be attributed to Ni$_3$P$_5$(PDF22-1190). When initial molar ratio of P/Ni was increased to 6/1 or 8/1, the characteristic peaks at 20 of 40.8°, 44.6°, 47.3°, 54.4° can be attributed to Ni$_3$P (PDF03-0953). The results shows the as-prepared products tend to transform into Ni$_3$P from Ni$_3$P$_5$ with initial molar ratio of p/Ni increased. The smallest molar ratio of p/Ni for synthesis of Ni$_3$P$_5$ is 4/1, while for synthesis of Ni$_3$P is 6/1 or 8/1.

3.2. The influence of hydrothermal temperature

The XRD patterns of as-prepared products (figure 2) shows the effect of hydrothermal temperature ranging from 90°C to 180°C on the crystal phase of as-prepared products. The molar ratio of p/Ni and hydrothermal temperature was fixed at 6 and 12 h. When the hydrothermal temperature is at 90°C, the strong peaks at 20 of 40.8°, 44.6°, 47.3°, 54.4° occurred, which can be attributed to Ni$_3$P (PDF03-0953), but accompanied with the weak characteristic peaks of Ni$_3$P$_5$ at 20 of 38.4°, 49.0°, suggesting the main product is Ni$_3$P while a small amount of Ni$_3$P$_5$ is also present. When the hydrothermal temperature is at 120°C, the characteristic peaks of Ni$_3$P are sharper while no other peaks can be observed, indicating high purity and crystallinity of as-prepared Ni$_3$P catalysts. When the hydrothermal temperature is at 150°C, the characteristic peaks of Ni$_3$P$_5$ occurred while there is a weak characteristic peak of Ni$_3$P at
2θ of 40.8°, indicating the main product is Ni$_{12}$P$_5$ while there is trace of Ni$_3$P. When the hydrothermal temperature is at 180°C, the position of peaks are basically the same as that at 150°C, however, the characteristic peaks of Ni$_3$P disappear, indicating the high purity of as-prepared Ni$_{12}$P$_5$. Therefore, the effect of hydrothermal temperature on the crystal phase of as-prepared products is great, the increment of hydrothermal temperature is in favor of the transformation of Ni$_{12}$P$_5$ from Ni$_3$P phase.

![XRD patterns of samples prepared for different n(P)/n(Ni).](image1)

**Figure 1.** XRD patterns of samples prepared for different n(P)/n(Ni).

![XRD patterns of samples prepared at different temperature for P/Ni=8.](image2)

**Figure 2.** XRD patterns of samples prepared at different temperature for P/Ni=8.

3.3. *Analysis of TEM images and textural properties*

Figure 3 shows the TEM images of Ni$_{12}$P$_5$ and Ni$_3$P catalysts. As is shown in figure 3(a) that the morphology of as-prepared Ni$_{12}$P$_5$ presents clustered aggregates composed of a large number of spherical particles, the size of which is almost micron level. As is shown in figure 3(b) that the morphology of as-prepared Ni$_3$P particle spread out more evenly, the size of which is about 20 nm. Besides, the BET specific surface area result of Ni$_{12}$P$_5$ and Ni$_3$P is 2.70m$^2$/g and 4.21m$^2$/g, respectively. Generally, the larger specific surface area is, the higher contact area is, and the higher absorption ability and photocatalytic degradation ability of catalysts will be owing to quantum size effect.
3.4. Photocatalytic degradation activity of Ni\textsubscript{12}P\textsubscript{5} and Ni\textsubscript{2}P catalysts

Figure 4 shows that the photocatalytic degradation rate of Ni\textsubscript{12}P\textsubscript{5} and Ni\textsubscript{2}P catalysts for methylene blue with reaction time. As is shown that the degradation rate is less than 7.12% when the catalysts is absent. In the presence of Ni\textsubscript{12}P\textsubscript{5} or Ni\textsubscript{2}P catalyst, the degradation rate gradually increase and reach constant at 210 min, the photocatalytic degradation rate of Ni\textsubscript{12}P\textsubscript{5} and Ni\textsubscript{2}P catalysts is 79.74% and 85.90%, respectively, indicating the as-prepared products have better photocatalytic degradation ability. After reaction finished, the solid catalyst could be easily recovered by simple filtration. The catalytic activity of the recovered catalysts almost unchanged. Correspondingly, the XRD patterns of that were the same as the fresh catalysts, indicating the structures of the recovered catalysts were still retained.

Figure 3. TEM images of as-prepared product for different molar ratio of P to Ni (a) Ni\textsubscript{12}P\textsubscript{5} (n(P)/n(Ni)=4/1) (b) Ni\textsubscript{2}P (n(P)/n(Ni)=8/1).

4. Conclusions

Ni\textsubscript{2}P and Ni\textsubscript{12}P\textsubscript{5} can be controllably synthesised achieved by changing the molar ratio of P/Ni and reaction temperature. The increment of molar ratio of P/Ni is advantageous to transform the tetragonal Ni\textsubscript{12}P\textsubscript{5} phase into hexagonal Ni\textsubscript{2}P phase, while the increment of thermal temperature is advantageous to transform the hexagonal Ni\textsubscript{2}P phase into the tetragonal Ni\textsubscript{12}P\textsubscript{5} phase. Compared with Ni\textsubscript{12}P\textsubscript{5}, Ni\textsubscript{2}P shows the better photocatalytic degradation ability for methylene blue, which of Ni\textsubscript{12}P\textsubscript{5} and Ni\textsubscript{2}P is 79.74% and 85.90 %, respectively.

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