

Rapid communication

Synthesis of supported bimetal phosphide catalysts based on red phosphor and hydrodesulfurization property



Limin Song^{a,*}, Shujuan Zhang^{b,*}, Xiaoqing Wu^{c,*}, Kai Wang^a

^a College of Environment and Chemical Engineering & State Key Laboratory of Hollow-Fiber Membrane Materials and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, PR China

^b College of Science, Tianjin University of Science & Technology, Tianjin 300457, PR China

^c Institute of Composite Materials, Tianjin Polytechnic University, Tianjin 300387, PR China

ARTICLE INFO

Article history:

Received 2 October 2014

Received in revised form

28 October 2014

Accepted 3 November 2014

Available online 11 November 2014

Keywords:

Nickel cobalt phosphide

Red phosphor

Hydrodesulfurization

Dibenzothiophene

ABSTRACT

Silica-supported NiCoP (NiCoP/SiO₂) catalysts were prepared by reducing nickel chloride (NiCl₂·6H₂O) and cobalt chloride (CoCl₂·6H₂O) with red phosphor (P) precursors. Physicochemical properties were determined by inductively coupled plasma spectroscopy, N₂ adsorption experiment, X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy, and differential scanning calorimetry. Catalytic activities against the hydrodesulfurization of dibenzothiophene were evaluated in a fixed-bed reactor in flowing H₂. The as-prepared NiCoP/SiO₂ catalyst exhibited high hydrodesulfurization activities and selectivity for indirect hydrodesulfurization (>90%).

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As an important environmental issue in the refining industry [1], removal of sulfur in fuels has been allowed by oxidative desulfurization, biodesulfurization and hydrodesulfurization (HDS) [2,3], with CoMo or NiMo sulfides as the main HDS catalysts conventionally [4,5]. In recent years, transition metal phosphides, including single metal phosphides of Ni₂P [6,7], CoP [8,9], FeP [10], MoP [11], have become novel efficient catalytic materials for HDS [12,13]. Besides, bimetal phosphides have superior HDS activity and selectivity to those of single metal phosphides [14–21]. Oyama et al. reported a bimetallic NiFe phosphide catalyst with higher activity than those of commercial catalysts [17] and high selectivity for direct desulfurization. Burns et al. reported unsupported and supported Co_{0.08}Ni₂P catalysts with higher activities than that of pure Ni₂P catalysts [18]. Bussell et al. also found Fe_xNi_{2-x}P_y catalysts showed high activities in HDS [19]. Moreover, Ni₂P was endowed an unexpected catalytic performance by adding excess metals. In this study, a NiCoP/SiO₂ catalyst was successfully prepared using red phosphor. The mechanism for NiCoP formation was discussed in detail. In the HDS of dibenzothiophene (DBT), the conversion of

sulfur reached 83% and the selectivity of indirect HDS exceeded 90% at 320 °C over the as-prepared NiCoP/SiO₂.

A typical synthetic route: NiCl₂·6H₂O (2.0 g) and CoCl₂·6H₂O (2.0 g) were dissolved in 50 mL of deionized water, to which was added 3.7 g nano-silica (479 m²/g, mean diameter: 15 nm) carrier, and the resultant solution was stirred for 3 h. The mixture was evaporated at 85 °C in a water bath in order to obtain the precursor. Then red phosphorus (0.53 g) and the above precursor (5.04 g) were mixed and directly heated to 700 °C for 1 h in a N₂ atmosphere in a tube furnace (the molar ratio of Ni/Co/P = 1:1:6). Finally, the reaction was cooled to room temperature. The samples were passivated for 1 h in a flow of 1 vol% O₂/N₂. The as-obtained sample was ground to powders. For unsupported NiCoP, the mixture of NiCl₂·6H₂O (2.0 g), CoCl₂·6H₂O (2.0 g), and red phosphorus (0.53 g) was directly heated to 700 °C for 1 h in a N₂ flow (the molar ratio of Ni/Co/P = 1:1:6). A traditional synthetic route (Temperature-programmed reduction (TPR) method): Co(NO₃)₃·6H₂O (1.0 g) and Ni(NO₃)₂·6H₂O (1.0 g) were dissolved in 20 mL deionized water. The nano-silica (479 m²/g, mean diameter: 15 nm) was impregnated in an aqueous solution of Co(NO₃)₃·6H₂O and Ni(NO₃)₂·6H₂O for 3 h, followed by drying at 120 °C for 4 h. The dried solid was subsequently impregnated in a NH₄H₂PO₄ (0.47 g in 10 mL deionized water) solution for 3 h, followed by drying at 120 °C for 4 h, and

* Corresponding authors. Tel./fax: +86 22 83955458.

E-mail addresses: songlimin@tjpu.edu.cn, songlmink@sohu.com (L. Song).

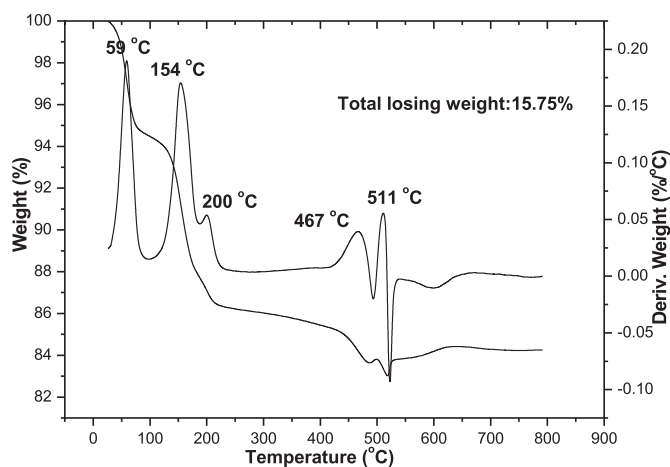


Fig. 1. TG/DTG analysis of the NiCoP/SiO₂ (Ni: 10 wt.%, Co: 10 wt.%) prepared at 700 °C for 1 h.

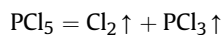
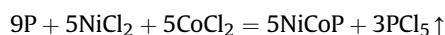
calcination at 500 °C for 3 h. The above solid powder was reduced for 2 h at 650 °C in a 200 mL/min H₂ at a rate of 1 K/min [17,18]. Finally, the furnace was cooled to room temperature. The samples were passivated for 1 h in a flow of 1 vol% O₂/N₂. The as-prepared product was ground to 20–40 mesh powders.

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max 2500 X-ray diffractometer. Morphological analysis was performed with a JEM 2010 transmission electron microscope (TEM) at an acceleration voltage of 200 kV. Thermogravimetric mass spectrometer (TG-MS) analysis was carried out to evaluate the preparation process in N₂ (15 mL/min) using a STA409PC-QMS403 simultaneous analyzer. Fourier transform infrared (FT-IR) spectra were recorded using a Tensor37 Bruker infrared spectrometer. Brunauer–Emmett–Teller (BET) surface area was measured by a Micromeritics ASAP2020 automatic surface area analyzer. The element compositions of the samples were characterized using a Varian 715-ES inductively coupled plasma atomic emission spectrometer (ICP-AES). The products of hydrodesulfurization were studied on an Agilent 7890A/5975C gas chromatograph-mass spectrometer (GC-MS).

HDS of DBT was conducted at 320 °C and 3.0 MPa by a home-made fixed-bed flow reactor. In brief, 20–40 mesh catalyst (0.6 g, 1.0 mL) was mixed with 4.0 mL of 20–40 mesh quartz sands and heated to 400 °C (20 °C/min) in a H₂ stream (200 mL/min) for 3 h to reduce the catalyst surface. Then 0.5 wt.% of DBT decalin solution was introduced into the reactor at 9 mL/h at 320 °C. The products were analyzed by gas chromatograph (flame ionization detector, FID) equipped with OV101 columns.

TG-DTG analyses of the NiCl₂·6H₂O, CoCl₂·6H₂O and red P precursor were performed in the range of 20–800 °C to clarify the preparation process of NiCoP. As shown in Fig. 1, there are four important endothermic peaks. The endothermic peak at 59 °C results from the evaporation of water adsorbed on the surface of materials. The two endothermic peaks at 154 °C and 155 °C can be assigned to the losses of crystallization water of NiCl₂·6H₂O and CoCl₂·6H₂O respectively, accompanied by a mass loss of 13.9%. The

two endothermic peaks at 461 °C and 511 °C indicate that there are reactions between NiCl₂·6H₂O, CoCl₂·6H₂O and red P, accompanied by the weight loss of about 1.85%. In order to investigate the mechanism for NiCoP formation, TG-MS analysis was carried out. According to the TG-MS result, the main gaseous products are H₂O, PCl₅, PCl₃, P₄, and Cl₂ in Table 1. The melting point of red P is 590 °C. The red P formed P₄ (white P) at high temperature. The produced H₂O results from crystal water or water adsorbed on the materials surface. The reaction of red P and metal chlorides is to produce NiCoP and PCl₅. Under high temperature, PCl₅ can be decomposed to form Cl₂ and PCl₃. Therefore, the chemical reaction progresses in the solid phase following the equation below:



Phase structure and crystallinity of NiCoP/SiO₂ obtained at 700 °C for 1 h were determined by XRD in Fig. 2. The amorphous peak at 22° in Fig. 2 is assigned to the SiO₂ support. The existence of NiCoP phase in Fig. 2 is verified by the characteristic peaks at 40.99°, 44.90°, 47.58°, 54.44°, 54.74°, 66.69°, 70.34°, 73.15°, and 75.41°, which represent the (111), (201), (210), (300), (002), (310), (221), (311), (212) planes of hexagonal NiCoP (JCPDS file no. 71-2336), respectively. There were no obvious impurities in Fig. 2 when the molar ratio of Ni/Co/P was 1:1:3. The diffraction peaks are sharp and strong, indicating a high degree of crystallinity of NiCoP phase when the molar ratio of Ni/Co/P was 1:1:6. At the same time, no signals of other impurities were detected. Therefore, SiO₂ supported NiCoP had been successfully synthesized using red phosphorus and metal salts with the Ni/Co/P molar ratio of 1:1:6. The additional sharp XRD peaks were found in Fig. 2 when the molar ratio of Ni/Co/P was 1:1:9 and 1:1:12. The result exhibits that excess phosphorus can product impurities, therefore, we selected the mole ratio is 1:1:6 during the synthesis.

Morphology and size of NiCoP/SiO₂ obtained at 700 °C for 1 h were observed by transmission electron microscopy. In Fig. 3(a), the gray small particles are the SiO₂ support, and the black large particles are the NiCoP phase. Some NiCoP particles aggregate

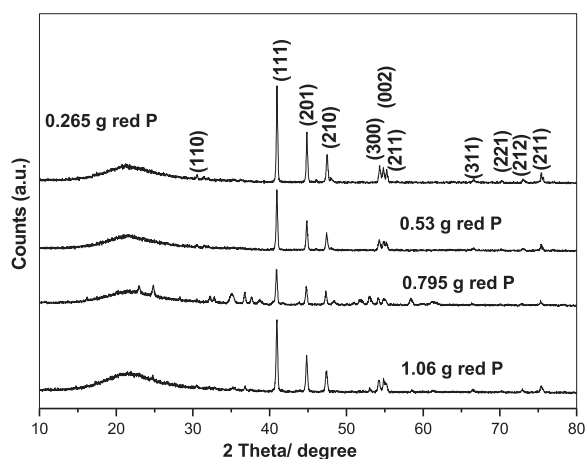


Fig. 2. X-ray diffraction patterns of NiCoP/SiO₂ prepared by controlling the variable concentration of red P. (Ni: 10 wt.%, Co: 10 wt.%).

Table 1

TG-MS analysis of the main products during the preparation of NiCoP/SiO₂ (Ni: 10 wt.%, Co: 10 wt.%).

Main products	H ₂ O	PCl ₅	PCl ₃	P ₄	Cl ₂

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