

Research Note

Preparation and hydrotreating activity of unsupported nickel phosphide with high surface area

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Abstract

An unsupported nickel phosphide catalyst with high surface area ($130 \text{ m}^2/\text{g}$) and high hydrotreating activity was prepared in the presence of a polymer surfactant (Triton X-114) and ethylene glycol. The resulting catalyst was characterized by XRD, SEM, TEM, CO and O₂ chemisorption, and ³¹P MAS NMR spectroscopy. Both polymer surfactant and ethylene glycol are necessary to obtain good texture properties and hydrotreating activities of bulk nickel phosphide catalysts.

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1. Introduction

Recent studies have shown that metal phosphides of Mo, W, Co, and Ni can be prepared from the corresponding metal salts and (NH₄)₂HPO₄ by reduction in H₂ and that the resulting materials have high hydrotreating activities [1–12]. Among the transition metal phosphides tested, Ni₂P/SiO₂ has demonstrated the highest hydrodesulfurization (HDS) activity [9]. However, the high temperatures needed in the reduction method (because the P–O bond is strong and its reduction requires high temperature) lead to a low dispersion and relatively low catalytic activity of the resulting catalysts. In previous studies, we used PH₃ to prepare silica and alumina-supported Ni₂P and MoP with high dispersion and catalytic activity at moderate temperatures [13–15]. Another way to improve the activity of the phosphide catalyst would be to prepare bulk metal phosphides with high surface area. Polymer surfactants have been used successfully for the preparation of mesoporous materials [16]. Recently it was reported that highly dispersed unsupported NiMo and CoMo sulfides can be prepared by using nonionic surfactants [17]. In the present study, we developed a surfactant-assisted method based on the classical phosphate re-

duction method to prepare bulk Ni₂P catalyst with high surface area and activity.

2. Experimental

2.1. Catalyst preparation

The preparation of bulk Ni₂P catalyst was carried out by preparing the Ni phosphate precursor (precatalyst) in aqueous solution and reducing it in flowing H₂. All of the chemicals were purchased from Fluka. In a typical preparation, 30 mL of Triton X-114 (polyethylene glycol *tert*-octylphenyl ether, abbreviated as Triton) and 100 mL of ethylene glycol (EG) were added to 50 mL of an aqueous solution of 5.8 g Ni(NO₃)₂ · 6H₂O under stirring at room temperature (RT), and the mixture was stirred for another 0.5 h. Then an aqueous solution of 2.64 g (NH₄)₂HPO₄ in 100 mL of water was added under stirring. The resulting precipitate was separated by filtration and dried at 393 K overnight. Surplus P was used in the precatalyst (molar ratio of P:Ni = 1), because normally some loss of P occurs during the reduction [7]. The dried powder was reduced in a flow of H₂ (150 mL/min) while increasing the temperature from RT to 673 K at a rate of 2 K/min and from 673 to 773 K at a rate of 1 K/min and then keeping the temperature at 773 K for 2 h. Then the samples were cooled to 298 K in flowing H₂,

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flushed with He for 20 min, and passivated in a flow of 1 mol% O₂/He. For comparison, samples were prepared in the absence of Triton and EG (referred to as blank).

2.2. Characterization

XRD measurements were carried out on a STOE STADI P powder diffractometer (Cu-K α radiation, Ge monochromator, PSD detector). The samples were put into a 0.3-mm-diameter capillary, which was rotated during measurement. The particle size of nickel phosphide was calculated using Scherrer's equation, $d = 0.9\lambda/\beta \cos \theta$.

Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2010 instrument. Approximately 0.2 g of sample was degassed at 473 K overnight before the measurement. The surface area was determined according to the BET method. CO and O₂ chemisorption analyses were performed as described elsewhere [13].

The morphology and the particle size of the samples were studied by scanning electron microscopy (SEM) on a Leo 1530 Gemini microscope operated at 20 kV and transmission electron microscopy (TEM) on a Philips CM30ST microscope operated at 300 kV (LaB6 cathode). For the TEM measurement, the material was deposited onto a perforated carbon foil supported on a copper grid.

2.3. HDS activity measurements

The HDS of dibenzothiophene (DBT) was carried out in continuous mode in a fixed-bed reactor as described elsewhere [11,18]. A 0.2-g sample of passivated catalyst was diluted with 8 g of SiC to achieve isothermal plug-flow conditions. The catalyst was activated in situ in H₂ (100 mL/min) at 673 K for 3 h to remove the passivation layer. After activation, the pressure was increased to 3.0 MPa and the temperature decreased to 613 K for the HDS reaction. The liquid reactant was fed into the reactor by means of a high-pressure pump. The composition of the gas-phase feed was 130 kPa of toluene (solvent), 8 kPa of dodecane (GC reference for DBT and its derivatives), 1 kPa of DBT, and 2.86 MPa of H₂. The catalyst was stabilized at 613 K and 3.0 MPa for at least 24 h before samples were obtained for analysis.

3. Results and discussion

XRD demonstrated that all of the precatalysts were amorphous and that reduction in flowing H₂ resulted in the formation of crystalline nickel phosphides. For the blank sample (prepared in the absence of Triton and/or EG), a mixture of Ni₂P and Ni₅P₄ was obtained after reduction in H₂ at 773 K for 2 h (Fig. 1a). For samples prepared in the presence of Triton and/or EG (with samples named Triton, EG, and Triton-EG), only diffraction peaks of Ni₂P were obtained in the XRD patterns after reduction in H₂ at 773 and 873 K. Fig. 1b showed that besides Ni₂P, another phase, Ni₁₂P₅, was also present in the Triton-EG sample when the reduction temperature was decreased to 723 K. Similar results were obtained for samples with a P/Ni

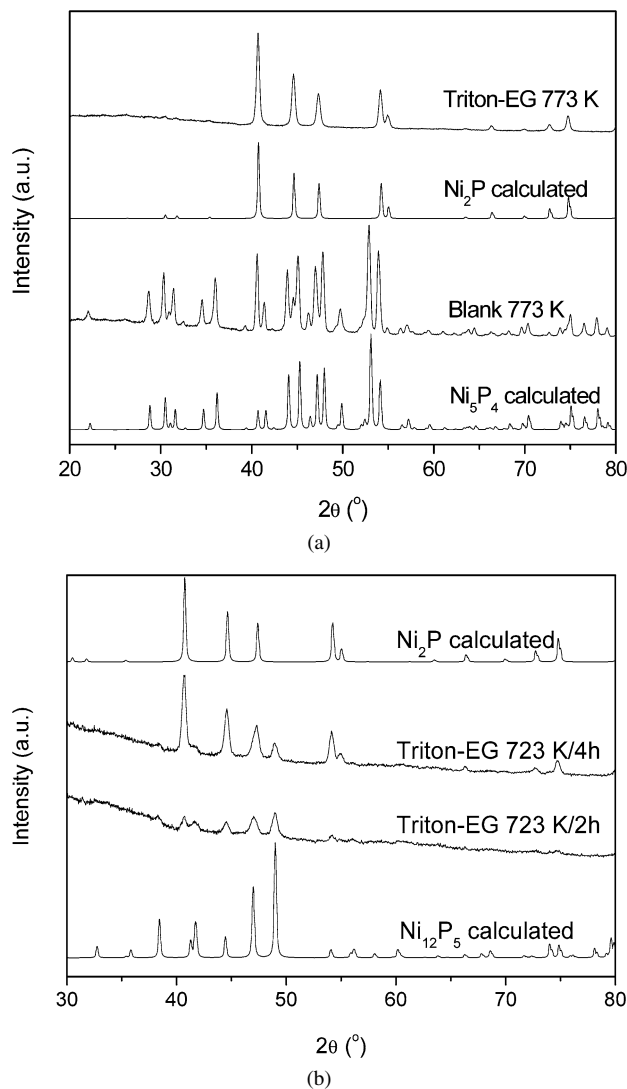


Fig. 1. (a) XRD patterns of the sample prepared in the absence of Triton and EG (blank) and the sample prepared in the presence of Triton and EG (Triton-EG) after reduction in H₂ at 773 K for 2 h and the calculated patterns of Ni₂P and Ni₅P₄. (b) XRD patterns of the sample prepared in the presence of Triton and EG after reduction in H₂ at 723 K for 2 and 4 h and calculated patterns of Ni₂P and Ni₁₂P₅.

ratio of 0.5. Table 1 lists the crystallite sizes calculated using Scherrer's equation for the (111) diffraction of Ni₂P, the (303) diffraction of Ni₅P₄, and the (312) diffraction of Ni₁₂P₅, as well as the BET surface areas of these samples.

Table 1 indicates that the addition of Triton and EG gives rise to a significant increase in the surface area of the resulting material. Sample Triton-EG reduced at 773 K has the highest surface area (130 m²/g), whereas the blank sample has a surface area of only 5 m²/g. It can be concluded that both surfactant and EG are needed to obtain good textural properties of the bulk Ni₂P catalysts. Table 2 shows that some residual carbon remained after reduction in H₂ in the samples prepared in the presence of Triton and/or EG. We propose that some Triton and EG remained in the precatalysts and was transformed to carbonaceous species on reduction in H₂ at higher temperatures. These carbonaceous species could be well dispersed around the Ni₂P particles, preventing them from sintering.

Table 1
Preparation conditions and properties of the catalysts

Sample	Reduction temperature (K)	XRD		S_{BET} (m^2/g)
		Phase	Size (nm)	
Blank	773	Ni_2P	31	5
		Ni_5P_4	27	
Triton	873	Ni_2P	28	15
Triton	773	Ni_2P	27	56
EG	773	Ni_2P	25	70
Triton-EG	723	Ni_2P	22	186
		Ni_{12}P_5	16	
Triton-EG	773	Ni_2P	23	130
Triton-EG	873	Ni_2P	28	24

From the crystallite size, we can calculate an effective surface area by using the equation $S = 6/D_c\rho$ ($\rho_{\text{Ni}_2\text{P}} = 7.09 \times 10^6 \text{ g/m}^3$) of the crystallites, assuming cubic or spherical geometry [7]. The calculated surface area of sample Triton-EG reduced at 773 K is only $37 \text{ m}^2/\text{g}$, which is much lower than the experimental value ($130 \text{ m}^2/\text{g}$). The reason for this could be that the Triton-EG sample has a porous structure or contains some very small particles. The residual amorphous carbon may also contribute to the BET surface area, but because the content of residual amorphous carbon is only 1.6 wt% (Table 2), this contribution cannot be more than about $10 \text{ m}^2/\text{g}$. To further investigate the structure of the materials, SEM and TEM measurements were carried out.

SEM pictures showed that the blank sample (Fig. 2a) was composed of two types of particles: big particles of several μm and small particles of about 100 nm, which was confirmed by TEM (not shown). The SEM pictures of sample EG (not shown) and Triton-EG (Fig. 2b) reduced at 773 K showed homogeneous and porous structures. However, a higher-resolution TEM picture (Fig. 2c) showed that two types of particles existed in the Triton-EG sample reduced at 773 K: amorphous, small particles of 6–7 nm and big particles of about 50 nm. Therefore, we conclude that the majority of the surface area of the Triton-EG sample ($130 \text{ m}^2/\text{g}$) originated from the amorphous phase, according to the equation $S (\text{m}^2/\text{g}) = 846/D_c (\text{nm})$ for Ni_2P .

Electron diffraction (ED) was carried out on both the small and big particles present in the Triton-EG sample; the results showed that the small particles were amorphous and the large particles were crystalline. The d -values of the big crystalline particles measured by ED were essentially the same as those of Ni_2P observed by XRD. We were not able to determine the composition and structure of the amorphous phase. The NMR spectrum of this sample showed only the characteristics

of Ni_2P . Spot analyses by energy-dispersive X-ray spectroscopy (EDXS) were carried out on various particles, but no evident variation in the Ni/P/O ratio was detected; the Ni/P/O ratio was almost the same for the small and large particles. The presence of oxygen might be caused by the surface passivation after reduction in H_2 . Therefore, we assume that the small particles were composed of amorphous nickel phosphide.

Because $\text{Ni}_2\text{P}/\text{SiO}_2$ has the highest HDS activity among the nickel phosphides tested and Ni_{12}P_5 has a very low hydrotreating activity [7,8], the aim of our work was to develop a preparation method for unsupported Ni_2P with high surface area. Decreasing the reduction temperature to 723 K led to the formation of Ni_{12}P_5 , and therefore we increased the reduction temperature from 773 to 873 K. This resulted in pure Ni_2P , as well as a significant decrease in the surface area of the Triton-EG sample from 130 to $24 \text{ m}^2/\text{g}$. The TEM picture of this sample (Fig. 2d) shows that the small amorphous particles present in the sample reduced at 773 K (Fig. 2c), were not present when the reduction temperature was increased to 873 K. Instead, some small crystalline particles appeared, as confirmed by high-resolution TEM (Fig. 2e). Both XRD and ED results showed that only one crystalline phase, Ni_2P , was present in the Triton-EG sample reduced at 873 K.

The catalytic activities of the resulting samples in the HDS of DBT are listed in Table 2. The conversions of DBT were taken at a weight time [19] of 15 g min/mol. Fig. 3 presents the results of the HDS of DBT over the Triton-EG sample reduced at 773 (Fig. 3a) and 873 K (Fig. 3b). Both catalysts produced three reaction products: biphenyl (BP), cyclohexylbenzene (CHB), and tetrahydro-dibenzothiophene (THDBT). The product distribution indicates that DBT is desulfurized mainly through direct desulfurization (DDS) over both catalysts, as over $\text{Ni}_2\text{P}/\text{SiO}_2$ [14] and sulfided $\text{CoMo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$ catalysts [19]. Slow hydrogenation of BP to CHB occurred over both catalysts, because the BP selectivity decreased with weight time and the increase in the CHB selectivity with weight time was higher than the decrease in the THDBT selectivity.

The activity of the Triton-EG sample reduced at 773 K in the HDS of DBT is about twice that of the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts prepared by the PH_3 method [13,14] and about one order of magnitude higher than the activity of the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts prepared by the classical H_2 reduction method [13]. The HDS activity of sample Triton-EG reduced at 873 K was lower than the activity of the same sample reduced at 773 K. This may be caused by the large decrease in surface area due to the sintering at the higher reduction temperature. Another reason could

Table 2
Chemisorption, elemental analysis and HDS activity of the samples after reduction in H_2 at 773 K for 2 h

Sample	CO uptake ($\mu\text{mol}/\text{g}$)	O_2 uptake ($\mu\text{mol}/\text{g}$)	Carbon (wt%)	HDS of DBT			
				DBT Conversion (%)	Selectivity (%)		
					BP	CHB	THDBT
Blank	5	11	0.1	69	86	13	1
Triton	38	34	1.1	22	93	4	3
EG	–	–	2.4	42	91	7	2
Triton-EG	58	58	1.6	80	90	7	3

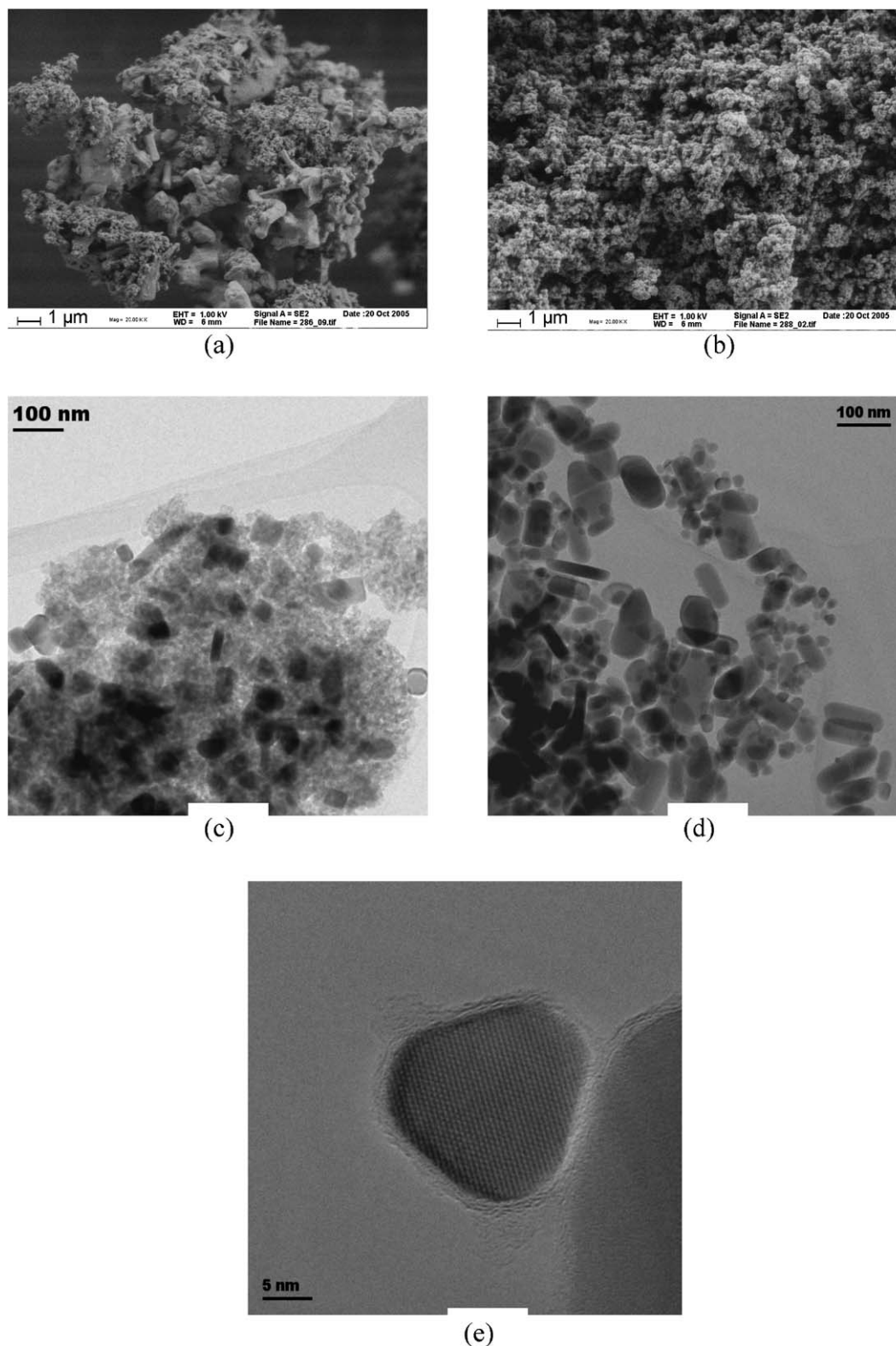


Fig. 2. SEM images of the blank sample (a) and sample Triton-EG reduced at 773 K (b) and TEM images of sample Triton-EG reduced at 773 K (c) and 873 K (d and e).

be that a carbonaceous layer had formed on the surface of the sample when reduced at 873 K (as shown in Fig. 2e), hindering the adsorption of DBT molecules onto the active sites of the catalyst.

4. Conclusion

An unsupported nickel phosphide catalyst with high surface area and high hydrotreating activity can be obtained by reduc-

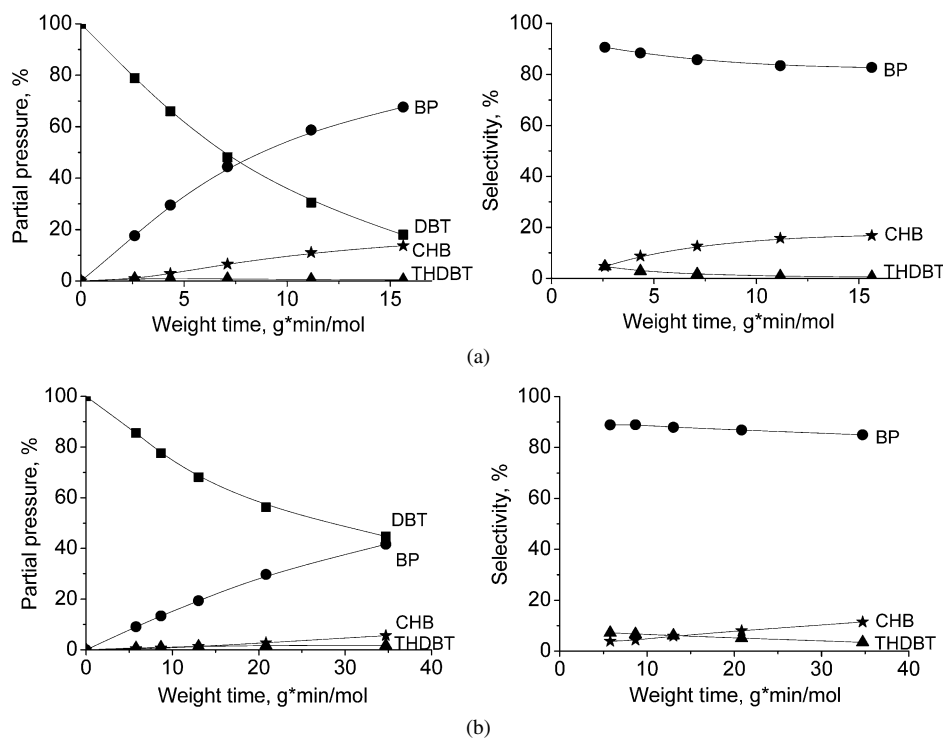


Fig. 3. Relative partial pressures and selectivities of the products of the HDS of DBT over sample Triton-EG reduced at 773 K (a) and 873 K (b).

tion of a metal phosphate precursor prepared in the presence of polymer surfactant (Triton X-114) and EG. The reduction temperature has a very significant effect on the catalytic activity of the resulting material. The HDS activity of the Triton-EG sample reduced at 773 K is much higher than that of the same sample reduced at 873 K.

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