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Short communication

The effect of neodymium content on dibenzothiophene HDS performance over a bulk Ni_2P catalyst

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ABSTRACT

Neodymium (Nd)-modified Ni_2P catalysts (Nd_xNi_2P, where x is the molar fraction of Nd to Ni_2P) have been successfully prepared. An appropriate amount of Nd can dramatically increase the surface area and promote the formation of smaller and highly dispersed Ni_2P particles. The Nd_xNi_2P catalyst with $x = 0.10$ exhibited the highest dibenzothiophene hydrodesulfurization activity of 97.4%, which is an increase of 35% when compared with that found for bulk Ni_2P.

1. Introduction

Driven by more and more stringent environmental regulations and the increasing use of heavy crude oil, sulfur removal from transportation fuels is becoming one of the acutest problems for the refining industry. Among the sulfur removal methods, hydrodesulfurization (HDS) has been widely used over the past decade. However, the current commercially used HDS catalysts are not up to the standard set by the regulations [1]. Hence, plenty of research has been performed to develop a new generation of replacement materials. Transition metal phosphides have received a lot of attention because of their high performance in HDS. The observed activity for transition metal phosphides in the HDS of dibenzothiophene (DBT) follows the general trend: $Fe_2P < CoP < MoP < WP < Ni_2P$ [1,2].

Rare earth metals exhibit excellent physical, chemical, optical and electrical properties because of their unfilled 4f electron shell [3]. Therefore, they have been continually employed and investigated as structural and electronic promoters to improve the performance of various catalysts [4]. The addition of CeO_2 to Ni_2P can significantly decrease the particle size of Ni_2P, and increase the specific surface area and CO adsorption properties, resulting in increased HDS activity [5,6]. Our previous work showed that yttrium (Y) incorporated in the bulk Ni_2P catalyst can increase the surface area of the catalyst, leading to a smaller crystallite size and better dispersion of the active Ni_2P particles [7].

In this paper, neodymium (Nd) element was successfully introduced into bulk Ni_2P and the effect of Nd content on the HDS performance of Ni_2P was studied.

2. Experimental

2.1. Preparation of catalysts

The unsupported Ni_2P catalysts were prepared by temperature programmed reduction (TPR) method reported by our previous study [7]. The oxidic precursor of bulk Ni_2P was prepared with excess phosphorus ($Ni{:}P = 1{:}1$) to compensating the loss of phosphorus during the reduction stage [8]. A mixture of $Ni(NO_3)_2$ and $(NH_4)_2 \cdot HPO_4$ solution was stirred and the water was evaporated to obtain a solid product. The resulting solid was dried at 120 °C for 12 h and calcined at 500 °C for 3 h to obtain the oxidic precursor (PNi_2P). Nd was incorporated into the bulk Ni_2P by impregnating the PNi_2P with a solution of $Nd(NO_3)_3$. The resulting solid was treated as PNi_2P to obtain the final oxidic precursor ($PNdNi_2P$). Finally, the PNi_2P and $PNdNi_2P$ were reduced and passivated as our previous study [7]. The corresponding catalysts are denoted as Ni_2P and Nd_xNi_2P, where x represents the molar fraction of Nd with respect to Ni_2P.

2.2. Characterization of catalysts

XRD analysis was carried out on a D/max-2200 PC-X-ray diffractometer using Cu $K\alpha$ radiation under the setting conditions of 40 kV, 30 mA, scan range from 10 to 80° at a rate of 10°/min. The typical physicochemical properties of catalysts were analyzed by BET method using

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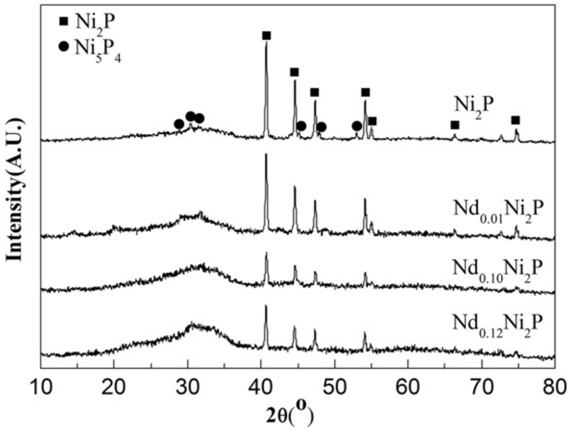

Fig. 1. XRD patterns of the Ni_2P and Nd_xNi_2P catalysts.

Micromeritics adsorption equipment of NOVA2000e. CO uptake measurements were performed in a Micromeritics ASAP 2010 apparatus under static volumetric conditions. The XPS spectra were acquired using ESCALAB MKII spectrometer.

2.3. Catalytic activities

The HDS of DBT over prepared catalysts was performed in a flowing high-pressure fixed bed reactor using a feed consisting of a decalin solution of DBT (1 wt.%). The conditions of the HDS reaction were 340 °C, 3.0 MPa, WHSV = 1.5 h^{-1}, and hydrogen/oil ratio of 500 (V/V). Prior to reaction, 0.8 g of the Nd_xNi_2P were pretreated in situ with flowing H_2 (40 mL/min) at 500 °C for 2 h. Sampling of liquid products was started 2 h after the steady reaction conditions had been achieved. The feed and reaction product was analyzed by FID gas chromatography with a GC-14C-60 column.

3. Results and discussion

3.1. XRD

The XRD patterns of all samples are shown in Fig. 1. For all samples, strong diffraction peaks at $2\theta = 40.6°$, 44.5°, 47.1° and 54.1° (PDF: 03-0953) can be attributed to the Ni_2P phase, which indicates that the active phase formed is mainly Ni_2P. The Ni_2P shows weak diffraction peaks at $2\theta = 28.8°$, 30.2°, 31.6°, 43.9°, 47.8° and 53.0° (PDF: 18-0883), which were ascribed to small amounts of the Ni_5P_4 phase. However, Nd_xNi_2P exhibits a broad peak owing to an amorphous phase at the corresponding position. This suggests that the addition of Nd to Ni_2P can suppress the formation of the Ni_5P_4 phase. It is worth noting that with an increasing Nd content in the catalysts, the Ni_2P phase peaks initially become more intense and broadened, and then become less intense. In general, an increase in the peak width exhibits a decrease in the crystallite size (D_c) of the Ni_2P. The crystallite sizes (D_c) (column 5 of Table 1), calculated from Scherrer's equation [9,10], initially decrease and then increase, reaching a minimum of 39 nm at $x = 0.10$, which shows an appropriate amount of Nd can promote smaller Ni_2P particles and a better dispersion of Ni_2P. Our previous work [5] studied the effect of the rare-earth metal (Y) on bulk Ni_2P. We found Y can greatly increase the surface area of the catalyst, promoting a smaller crystallite size (D_c) and better dispersion of active Ni_2P.

3.2. BET

Table 1 summarizes the textural properties of Ni_2P and Nd_xNi_2P. The surface area and pore volume of the Ni_2P catalysts were 11.17 $m^2 \cdot g^{-1}$ and 0.060 $cm^3 \cdot g^{-1}$, respectively. Upon increasing the Nd content, the specific surface area of Nd_xNi_2P showed a significant increase initially, reaching a maximum at $x = 0.1$ and then decreased with further increases in the Nd content. The surface area of the $Nd_{0.10}Ni_2P$ catalyst was 25.64 $m^2 \cdot g^{-1}$, which was an almost twofold increase when compared with that found for bulk Ni_2P. This indicates that an appropriate amount of Nd was beneficial to the formation of smaller and highly dispersed Ni_2P particles in the catalyst (see Table 1, column 5).

3.3. CO uptake

The CO uptake measurements were used to titrate the surface Ni atoms and to provide an estimate of the active CO uptake sites on the catalysts [8]. Although CO molecules may also be adsorbed P sites, their amount may be very small and they can be neglected [11]. The measured CO adsorption capacities at room temperature for all the samples are presented in column 6 of Table 1. The CO adsorption of the bulk Ni_2P sample was determined to be 171 $\mu mol \cdot g^{-1}$. The CO adsorption of the Nd_xNi_2P catalysts was dramatically higher than that of bulk Ni_2P, which showed that introducing Nd to the catalyst can improve the dispersion of active Ni_2P. The CO uptake of the $Nd_{0.12}Ni_2P$ catalyst was lower than that found for the $Nd_{0.10}Ni_2P$ sample. This was attributed to the decrease in surface area in $Nd_{0.12}Ni_2P$ upon increasing x from 0.10 to 0.12 (Table 1) because the surface area has a great effect on the dispersion of Ni sites. In addition, the excess Nd would occupy the some of the Ni sites leading to a decrease in the amount of exposed Ni sites on the catalyst's surface. This will be discussed further with the XPS analysis.

3.4. XPS

In order to gain further insight into the surface composition of the samples and the influence of Nd content, the XPS technique of samples was performed. The XPS spectra of the Ni_2P and Nd_xNi_2P samples in the Ni(2*p*) and P(2*p*) regions are shown in Fig. 2 and the binding energies are presented in Table 2. As shown in Fig. 2(a), all spectra were decomposed, taking into account the spin-orbital splitting of the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ lines (about 17 eV) and the presence of satellite peaks at about 5 eV higher than the binding energy of the parent signal [12]. For all catalysts, the bands centered at 852.1–852.7 eV and 856.1–856.7 eV can be attributed to the $Ni^{\delta+}$ species in the Ni_2P phase and Ni^{2+} species interacting with phosphate as a consequence of a superficial passivation, respectively [12,13]. As shown in Fig. 2(b), the peaks centered at 128.8–129.9 eV can be assigned to

Table 1
The textural characterization and HDS catalytic performance of the Ni_2P and Nd_xNi_2P catalysts.

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	V_p ($cm^3 \cdot g^{-1}$)	d (nm)	D_c[a] (nm)	CO uptake ($\mu mol \cdot g^{-1}$)	Conversion (%)	Selectivity (%)		TOF ($10^{-3} \cdot s^{-1}$)
							CHB	BP	
Ni_2P	11.17	0.060	21.7	54	171	62.1	35	65	8.5
$Nd_{0.01}Ni_2P$	14.10	0.066	20.2	50	229	75.9	32	68	7.3
$Nd_{0.10}Ni_2P$	25.64	0.129	18.7	39	326	97.4	31	69	6.5
$Nd_{0.12}Ni_2P$	15.13	0.074	19.6	43	291	89.5	33	67	6.9
$Y_{0.10}Ni_2P$	16.0	0.086	20.1	21	314	92.0	28	72	6.9

[a] Calculated from the $Dc = K\lambda/\beta \cos(\theta)$ (Scherrer equation) based on the Ni_2P {1 1 1}.

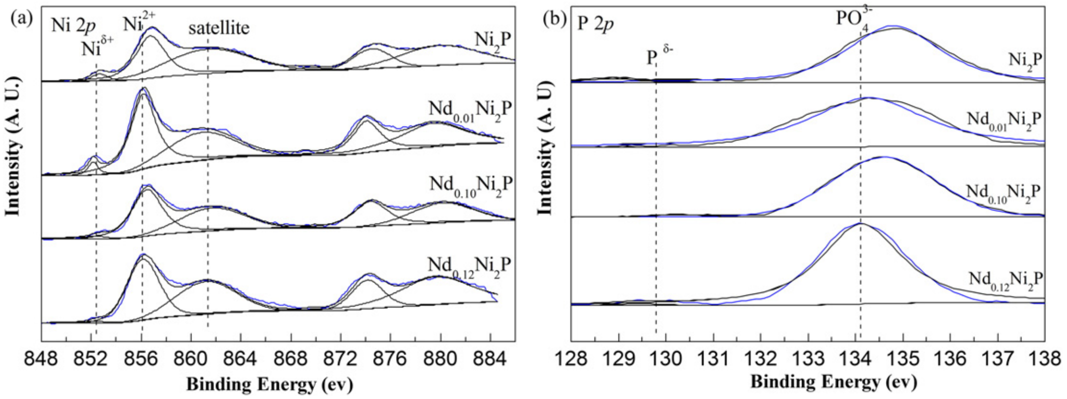

Fig. 2. XPS spectra of the Ni_2P and Nd_xNi_2P catalysts.

$P^{\delta-}$ species in the Ni_2P phase [12] and the peak at 134.1–134.8 eV can be attributed to phosphate (P^{5+}) due to superficial oxidation of the Ni_2P particles [14,15].

XPS analyses for the Ni_2P and Nd_xNi_2P catalysts were used to calculate the surface $Ni^{\delta+}/\Sigma Ni$ and P/Ni atomic ratios (Table 2). The $Ni^{\delta+}/\Sigma Ni$ ratios of the samples increased with Nd content, reaching a maximum at $x = 0.10$ and then decreased. This indicates that the addition of an appropriate amount of Nd promotes the formation of active Ni_2P, which improves the performance of the catalysts. Moreover, the P/Ni molar ratio of the Nd_xNi_2P samples were lower than that found for bulk Ni_2P, which indicates that the addition of Nd to Ni_2P can suppress the enrichment of P on the surface. The result obtained gives rise to more nickel sites being exposed on the surface of the samples, which may also influence the catalysts' performances.

Table 2
Spectral parameters obtained by XPS analysis.

Sample	Binding energy (eV)					Superficial atomic ratio	
	Ni $2p_{3/2}$			P $2p_{3/2}$			
	Ni^{2+}	Satellite	$Ni^{\delta+}$	P^{5+}	$P^{\delta-}$	$Ni^{\delta+}/\Sigma Ni$	P/Ni
Ni_2P	856.7	861.2	852.7	134.8	128.8	0.041	3.0
$Nd_{0.01}Ni_2P$	856.2	860.9	852.1	134.2	129.2	0.043	2.8
$Nd_{0.10}Ni_2P$	856.4	861.7	852.5	134.6	129.9	0.055	2.2
$Nd_{0.12}Ni_2P$	856.1	861.2	852.4	134.1	129.4	0.047	2.3

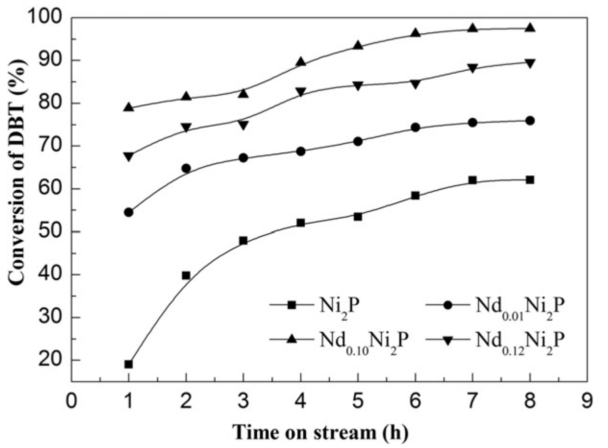

Fig. 3. The HDS activity of the Ni_2P and Nd_xNi_2P catalysts. Temperature, 340 °C; pressure, 3.0 MPa; H_2/oil ratio, 500 (V/V); WHSV, 1.5 h^{-1}.

3.5. HDS activity

As can be seen from Fig. 3, the HDS activities for all the catalysts gradually increased and then remained stable with time. The DBT conversion of bulk Ni_2P was only 62% after 8 h. The DBT conversion significantly increased and then decreased upon increasing the Nd content. The $Nd_{0.10}Ni_2P$ catalyst showed the maximum HDS activity of 97.4% after 8 h, an increase of 35% when compared with that found for Ni_2P. This was attributed to $Nd_{0.10}Ni_2P$ possessing smaller sized particles and a better dispersion of the active Ni_2P phase, as well as the higher surface area and lower coverage of phosphorus when compared with the other samples, which showed that an appropriate amount of Nd was beneficial for the HDS process.

The HDS activities, TOF and CO uptake of samples after reaction 8 h are presented in columns 6–10 of Table 1. The DBT conversion and TOF of bulk Ni_2P were 62% and 8.5×10^{-3} s^{-1}, respectively. Both the DBT conversion and CO uptake of Nd_xNi_2P increase very quickly, reaching a maximum at $x = 0.10$, and then decrease. On the contrary, variation of the TOF has a reverse trend. Hence, the higher CO uptake and lower TOF value were beyond that expected for the samples, which indicated that the metal sites do not accurately represent the actual active sites for HDS but just provide the initial active sites in HDS reaction [16]. The results obtained show that a nickel phosphosulfide active phase was generated during the HDS reaction [8,10].

The HDS catalytic selectivities of the catalysts are given in columns 8 and 9 of Table 1. For all the samples, the yield of BP is much higher than that of CHB, indicating that DBT primarily removed by the DDS pathway over all the catalysts [17]. Compared with Ni_2P, the selectivity to BP over Nd_xNi_2P is slightly higher, showing that the HDS route was not changed much by addition of Nd [18]. For comparison, the textural characterization and HDS activities of $Y_{0.10}Ni_2P$ reported in reference [7] are listed in line 7 of Table 1. It can be seen that the DBT conversion of $Nd_{0.10}Ni_2P$ with a higher CO uptake is obviously superior to that of $Y_{0.10}Ni_2P$, while the selectivity to BP over $Y_{0.10}Ni_2P$ is slightly higher than that of $Nd_{0.10}Ni_2P$.

4. Conclusions

In the present work, Nd-modified unsupported Ni_2P (Nd_xNi_2P) catalysts, which have higher HDS activity have been successfully prepared. XRD analysis indicated that the addition of Nd into the bulk Ni_2P can suppress the formation of the Ni_5P_4 phase and thereby promote the formation of the active Ni_2P phase. The crystallite size of Ni_2P first decreases, reaching a minimum at $x = 0.10$, and then increases upon increasing the Nd content. Moreover, the value of x has a large influence on the surface area of the catalyst and an appropriate amount of Nd ($x = 0.10$) was found to significantly increase the surface area, resulting in a better dispersion of the active Ni_2P phase. In addition, incorporation of an appropriate amount of Nd ($x = 0.10$) can suppress the enrichment of P on the surface of the catalyst and therefore increase the number of exposed nickel atoms, leading to the highest CO uptake. The $Nd_{0.10}Ni_2P$ catalyst exhibits the highest DBT HDS activity of 97.4%, which was an increase of 35% when compared with that found for bulk Ni_2P.

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