

Preparation of novel mesoporous Ce-Ni₂P/SBA-15 catalysts and their catalytic performance for hydrodesulfurization of dibenzothiophene

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Abstract Ni₂P/SBA-15 precursors with Ni₂P loadings of 25 wt% and initial P/Ni of 0.8 were prepared using nickel nitride as nickel source, diammonium hydrogen phosphide as phosphorus and mesopore molecular sieve SBA-15 as support. Then Ce was introduced into the Ni₂P/SBA-15 precursor. The novel mesoporous Ce-Ni₂P/SBA-15 catalysts were prepared after temperature-programmed reduction in flowing H₂. The structure was characterized by X-ray diffraction, N₂ adsorption–desorption isotherms, NH₃ temperature-programmed desorption and X-ray photoelectron spectroscopy. The catalytic activities for the hydrodesulfurization (HDS) of dibenzothiophene (DBT) were evaluated. The results showed that only Ni₂P phase was formed in Ce-Ni₂P/SAB-15 catalysts with Ce loadings of 0–5 wt%. Ni₂P and Ni₁₂P₅ phases were existed in 7 wt% Ce-Ni₂P/SBA-15 catalyst. The surface area and pore volume increased when Ce was added to Ni₂P/SBA-15 catalyst. The strength of the acid sites and total acid amount of Ce-Ni₂P/SBA-15 catalysts increased with increasing Ce loadings. Ce existed in the form of Ce³⁺ and Ce⁴⁺, Ni existed in the form of Ni²⁺ and Ni^{δ+}, and P existed in the form of P^{δ-} and P⁵⁺. The addition of Ce to the Ni₂P/SBA-15 catalyst decreased Ni^{δ+} concentration in Ni₂P/SBA-15 catalyst. The activity for HDS of DBT over Ni₂P/SBA-15 catalysts was affected by the addition of Ce at 300–340 °C. The catalysts exhibited a good catalytic performance of

deep hydrodesulfurization of dibenzothiophene and the conversion of DBT can reach 98.9 % at 380 °C. Biphenyl was the main product over Ce-Ni₂P/SBA-15 catalysts and cyclohexylbenzene was the main product over Ni₂P/SBA-15 catalyst at 380 °C.

Keywords Ce · Ni₂P · SBA-15 · Hydrodesulfurization · Dibenzothiophene

Introduction

Automobile industrial developments in the worldwide have increased the environmental pollution. Thus, the stricter standard for gasoline and diesel had been implemented, including decreased S content limits [1, 2]. Alumina-supported Mo or W sulfides by Ni or Co are mostly used as commercial hydrodesulfurization (HDS) catalysts on which dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are very difficult to remove [3]. So the novel high performance HDS catalysts are urgent to develop under the stringent legislation.

In the recent research, transition phosphides has been attracting attention as the next generation catalysts in the field of HDS, such as hydrogenation [4], hydrazine decomposition [5], especially hydrodesulfurization and hydrodenitrogenation [6, 7], due to their unique physical and chemical properties. Oyama et al. [8] reported that the activity of DBT HDS over Ni₂P/SiO₂ was higher than commercial Co–Mo sulfide catalysts. Mesopore molecular sieve belongs to regular channel structure that can promote large molecular diffusion in hydrocracking reaction. Wang et al. [9] had reported that the surface area and pore diameter of Ni₂P/MCM-41 were larger than that of Ni₂P/SiO₂ and Ni₂P/Al₂O₃ catalysts. It was also reported by

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Oyama that the catalytic performance for HDS of 4,6-DMDBT over Ni₂P/MCM-41 catalyst was higher than that of Ni₂P/SiO₂ catalyst [10]. Our previous work reported that Ni₂P/SBA-15 catalysts exhibited excellent deep activity of DBT HDS [11].

Hydrodesulfurization performance could be tunable by adding promoter to Ni₂P catalyst. Abu et al. [12] reported that the addition of Co to Ni₂P bulk catalyst brought an increase in 4,6-DMDBT HDS activity and selectivity. In previous paper [13], our group had reported the catalytic activity of Mo-Ni₂P/SBA-15/cordierite catalysts for DBT HDS, the addition of Mo to Ni₂P/SBA-15/Cordierite can promote the DBT activity and selectivity and the mechanism over Mo-Ni₂P/SBA-15/cordierite can be changed at 380 °C. It has been shown that cerium promoter could improve catalytic performance in some catalytic reactions. Li et al. [14] demonstrated that the influence of CeO₂ on hydrogenation activity over bulk Ni₂P. CeO₂ was an effective promoter enhancing the hydrogenation activity of 1-heptene and toluene over Ni₂P catalyst. Besides, Li et al. [15] also found that CeO₂ promoters could improve the activity of quinoline hydrodenitrogenation (HDN) over Ni₂P. Cai et al. [16] reported the effect of promoter Ce on the catalytic performance of Ni/Al₂O₃ catalyst for auto-thermal reforming of methane to hydrogen. The result showed that the addition of Ce to the Ni/Al₂O₃ catalyst increased the active surface that promoted the activity of the catalyst. In this study, the effect of Ce on DBT HDS over Ni₂P/SBA-15 catalyst is investigated. The relationship between the structures and catalytic activities of the catalysts are discussed.

Experimental

Preparation of catalyst

SBA-15 was synthesized using the literature method [17]. Ni₂P/SBA-15 precursors with P/Ni molar ratio of 0.8 were prepared by impregnating an aqueous solution of (NH₄)₂HPO₄ and Ni(NO₃)₂·6H₂O (add little HNO₃ if precipitation was formed) into SBA-15 for 12 h. Then dried at 120 °C for 24 h and subsequently calcined the sample at 550 °C for 4 h. The content of Ni₂P was about 25 wt%. Prior to H₂-TPR, the precursor was crushed to 40–60 mesh. 100 mL/min H₂ flow was used to reduce the precursor by heating from room temperature (RT) to 300 °C at 10 °C min⁻¹, then from 300 to 650 °C at 1 °C min⁻¹, and finally maintained at 650 °C for 2 h. After the reduction, the catalysts were cooled to RT and passivated by 1 % O₂/Ar (v/v) for structure characterization, or for HDS of DBT. Based on the above sample, Ce-Ni₂P/SBA-15 samples

were prepared by impregnating aqueous solutions of Ce(NO₃)₃·6H₂O with different concentration into the above Ni₂P/SBA-15 precursors at RT for 12 h, followed by drying the sample at 120 °C for 24 h and eventually calcining the sample at 550 °C for 4 h. The contents of Ce were 0–7 wt%.

Catalyst characterization

X-ray diffraction (XRD) patterns of Ce-Ni₂P/SBA-15 catalysts were obtained on a Rigaku D/Max 2500 VB2 +/PC diffractometer using Cu K α radiation operating at 200 mA and 40 kV. N₂ adsorption–desorption isotherms of Ce-Ni₂P/SBA-15 catalysts were measured using a Quadrasorb SI instrument. Before measurement, the sample was out-gassed for at least 5 h at 350 °C under vacuum. BET and BJH methods were used to determine the specific surface area and pore size distribution, respectively. NH₃-TPD data were collected from Thermo Electron TPD/R/O 1100 series catalytic surfaces analyzer equipped with a TC detector. Each sample was initially pretreated through heating in 20 ml/min of nitrogen from ambient to 300 °C, with a 1 h hold. The sample was then cooled down to ambient; ammonia adsorption was carried out. Physically adsorbed ammonia was removed by purging with nitrogen at 100 °C for 1 h. NH₃-TPD of the sample was carried out by increasing the temperature linearly from 40 to 800 °C with a heating rate of 10 K/min and a helium flow rate of 20 ml/min. XPS experiments were carried out on an ESCALAB 250 (Thermo Electron Co.) instrument using Al K α as the exciting radiation at constant pass energy of 30 eV. Binding energies were calibrated using the carbon present as a contaminant (C 1s = 285.0 eV).

Catalytic activity testing

The HDS of DBT was performed in a high-pressure fixed-bed continuous-flow stainless steel reactor (9 mm in diameter and 500 mm in length) with a central thermocouple to measure the temperature of the catalyst bed. Ce-Ni₂P/SBA-15 catalyst with different Ce loadings was loaded on the fixed-bed reactor between the pads of quartz sand. The reaction feed consisting of 1 wt% DBT in decalin was introduced into the reactor by a piston pump. The HDS reaction was operated at 3.0 MPa from 300 to 380 °C, liquid hourly space velocity = 1.9 h⁻¹, and the ratio of hydrogen-to-liquid feed was 400 (v/v). The liquid products were collected at 1 h intervals and analyzed by an off-line gas chromatography [SP2100, Beijing Beifenruili Analytic Instrument (Group) Co., Ltd], equipped with a flame ionization detector and a capillary column (HJ. PONA, 50 m × 0.20 mm × 0.50 μ m).

Results and discussion

XRD of Ce-Ni₂P/SBA-15 catalysts

Figure 1 shows the XRD patterns of Ce-Ni₂P/SBA-15 catalysts with different Ce loadings. In the case of Ni₂P/SBA-15 catalyst, the diffraction peak of the Ni₂P phase located at $2\theta = 40.6^\circ$, 44.5° , 47.3° and 54.1° (PDF-03-0953) had been observed, suggesting that Ni₂P was formed in the Ni₂P/SBA-15 catalyst. None of new diffraction peak appeared in the XRD patterns of Ce-Ni₂P/SBA-15 catalysts with $Ce \leq 5$ wt%. For 7 % Ce-Ni₂P/SBA-15 catalyst, the diffraction peak of the Ni₁₂P₅ phase appeared, which was located at $2\theta = 38.4^\circ$, 41.6° and 48.9° (PDF-22-1190). This indicated that Ni₂P and Ni₁₂P₅ phases existed in 7 % Ce-Ni₂P/SBA-15.

The diffraction peak of Ce species was not shown with the increasing of Ce loadings in Ce-Ni₂P/SBA-15 catalysts, indicating that Ce was well dispersed in SBA-15 or Ce concentration was too low. The result agreed with the literature [14]. Besides, No cerium phosphides (Ce₂Ni₁₂P₇ and CeNi₂P₂), cerium nickel phosphide (Ce₆Ni₆P₁₇) or cerium oxide species were observed when Ce was added to Ni₂P bulk catalyst. In the literature [18], the formation of Ni₁₂P₅ was attributed to the loss of phosphorus in temperature-programmed reduction process. It has reported by Abu et al. [12] that Ni₁₂P₅ and Ni₂P phases were formed due to the addition of excess Co to Ni₂P bulk catalyst. Therefore, it was thought that the addition of excess Ce to Ni₂P/SBA-15 catalyst inhibited enough phosphorus contacted with nickel to form Ni₂P phase. So in 7 % Ce-Ni₂P/SBA-15 catalyst, Ni₁₂P₅ phase was formed. Furthermore, the intensity of Ni₂P diffraction peaks was slightly

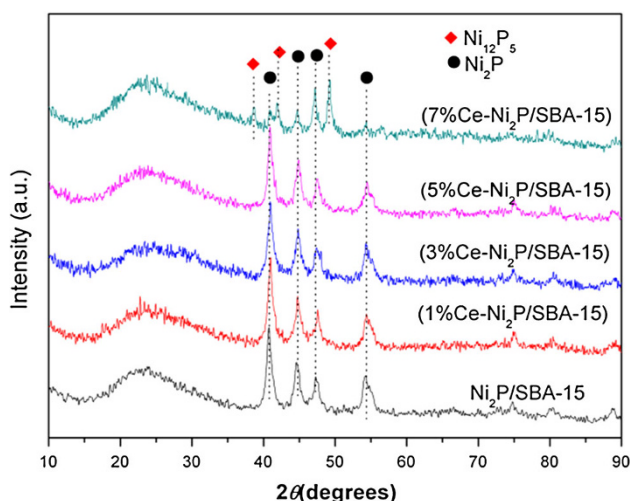


Fig. 1 XRD patterns of Ce-Ni₂P/SBA-15 catalysts with different Ce loadings

decreased with the increasing of Ce. This also corresponded to the previous research [19].

N₂ adsorption–desorption of Ce-Ni₂P/SBA-15 catalysts

N₂ adsorption–desorption isotherms of Ni₂P/SBA-15 and Ce-Ni₂P/SBA-15 catalysts are shown Fig. 2. It can be observed that the nitrogen adsorption–desorption isotherms of all catalysts were found to be of type IV according to IUPAC classification. All catalysts exhibited a H1 hysteresis loop that was a typical mesoporous solid [17]. This indicated that all catalysts retained SBA-15 mesoporous structure.

The pore structure parameters are summarized in Table 1. For Ni₂P/SBA-15 catalyst, the values of the S_{BET} , V_p and D_{BJH} were 247.8 m²/g, 0.30 m³/g and 3.8 nm, respectively. In the case of Ce-Ni₂P/SBA-15 catalysts, the values of S_{BET} and V_p were higher than that of Ni₂P/SBA-15 catalyst. It suggested that favorable influence on S_{BET} and V_p was shown by adding cerium in Ni₂P/SBA-15 catalyst. Abu et al. [12] recognized that the increased BET surface area of Co_xNi₂P and Co_{0.08}MoP suggested a reduction in the degree of agglomeration of the larger crystallites when the Co was added. Compared with 5 % Ce-Ni₂P/SBA-15 catalyst, the values of S_{BET} and V_p of 7 % Ce-Ni₂P/SBA-15 catalyst slightly decreased. This could be attributed to the dispersibility of active component which was weakened by adding the excess amount of cerium. However, the values of D_{BJH} were similar to that of Ni₂P/SBA-15 catalyst, which indicated that Ce-Ni₂P existed in the SBA-15 pore channel. Gutierrez et al. [20] recognized that desorption pore diameter of NiMo/Zr-SBA-15 catalysts was related with metal contents. The pore diameter

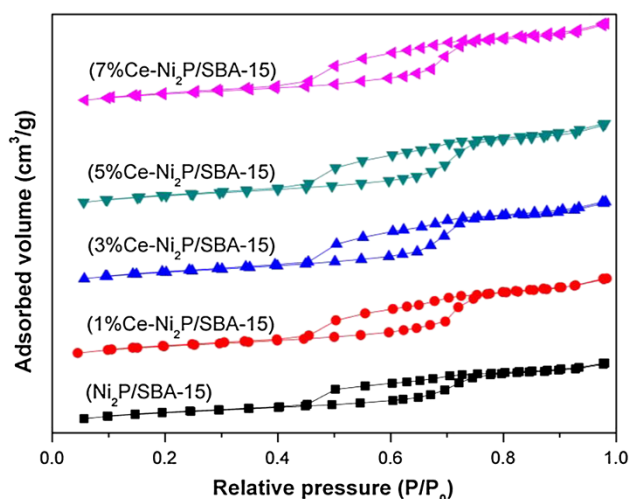


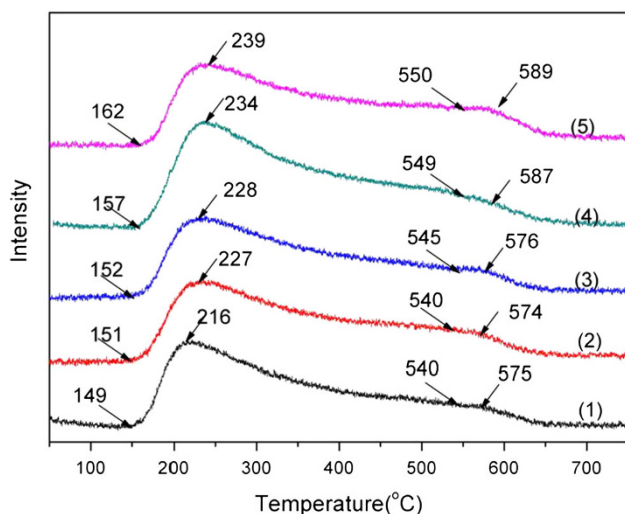
Fig. 2 N₂ adsorption–desorption isotherms of Ce-Ni₂P/SBA-15 catalysts with different Ce loadings

Table 1 Pore structure parameters of Ce-Ni₂P/SBA-15 catalyst with different Ce loadings

Catalysts	S_{BET} (m ² /g)	V_p (cm ³ /g)	D_{BJH} (nm)
Ni ₂ P/SBA-15	247.8	0.31	3.8
1 % Ce-Ni ₂ P/SBA-15	248.9	0.33	3.9
3 % Ce-Ni ₂ P/SBA-15	254.9	0.38	3.9
5 % Ce-Ni ₂ P/SBA-15	265.8	0.40	3.9
7 % Ce-Ni ₂ P/SBA-15	260.1	0.38	3.9

Table 2 NH₃-TPD results of Ce-Ni₂P/SBA-15 catalyst with different Ce loadings

Samples	Temperature (°C)		Acid amount (μmol/g)
	Weak acid	Strong acid	
Ni ₂ P/SBA-15	216	575	869
1 % Ce-Ni ₂ P/SBA-15	227	574	895
3 % Ce-Ni ₂ P/SBA-15	228	576	935
5 % Ce-Ni ₂ P/SBA-15	234	587	989
7 % Ce-Ni ₂ P/SBA-15	239	589	1,094

**Fig. 3** NH₃-TPD profiles of Ce-Ni₂P/SBA-15 catalysts with different Ce loadings / Ni₂P/SBA-15, 2 1 % Ce-Ni₂P/SBA-15, 3 3 % Ce-Ni₂P/SBA-15, 4 5 % Ce-Ni₂P/SBA-15, 5 7 % Ce-Ni₂P/SBA-15

was stable due to the metal existed in the Zr-SBA-15 channel when metal loadings were low, and the pore diameter decreases because high metal loadings blocked the SBA-15 pore mouth.

NH₃-TPD of Ce-Ni₂P/SBA-15 catalysts

Hydrodesulfurization activity and selectivity were related to acidity according to some investigates. In this work, the acidity of the Ce-Ni₂P/SBA-15 catalysts was investigated by temperature-programmed desorption of ammonia (NH₃-TPD). The technique provided information on the total acidity of the solid and strength of acid sites.

The NH₃-TPD profiles of Ce-Ni₂P/SBA-15 catalysts with different Ce loadings are presented in Fig. 3. It can be observed two desorption peaks on all NH₃-TPD curves. One was the large peak at lower temperature assigned to weak acid sites. The other was small peak at higher temperature assigned to strong acid site.

Generally, the acid sites were classified into the weak (≤ 200 °C), medium (200–350 °C) and strong (≥ 350 °C) acid sites [21]. With regard to Ni₂P/SBA-15 catalyst,

there were two peaks: the large desorption peak with the start desorption temperature at 145 °C and maximum desorption temperature at 216 °C, and the small desorption peak with the start desorption temperature at 540 °C and the maximum desorption temperature at 575 °C. Hu et al. [22] reported the desorption temperature at 114 °C of SBA-15 associated with Si–OH bond. Duan et al. [23] recognized that the metal atom in metal phosphide transferred into phosphorus atom resulting in the formation of acid site (252 and 620 °C). In the case of Ce-Ni₂P/SBA-15 catalysts, the start desorption temperature and the maximum desorption temperature are shifted to higher temperature with the increasing of Ce loadings. This suggested that the strength of acid sites of Ce-Ni₂P/SBA-15 catalysts was higher than that of Ni₂P/SBA-15 catalyst. Kalita et al. [24] reported that the strength of acid was related to desorption temperature. With the increasing of the desorption temperature, the strength of acid increased.

The total acid amount values are given in the Table 2. The value of Ni₂P/SBA-15 catalyst was 869 μmol/g, and the values of Ce-Ni₂P/SBA-15 catalysts increased with increasing Ce, which showed that Ce could improve the acid amount of Ni₂P/SBA-15 catalyst. Yu et al. [25] reported that the Ce addition to the Pt–Sn/γ-Al₂O₃ catalyst can increase acid amount of Pt–Sn/γ-Al₂O₃ catalyst.

XPS of Ce-Ni₂P/SBA-15 catalysts

XPS spectra of Ce-Ni₂P/SBA-15 catalysts were shown in Fig. 4. As seen in the Fig. 4a are Ce3d5 spectra of Ce-Ni₂P/SBA-15 catalysts. The two binding energy (BE) peaks at 882.2 and 884.6 eV are assigned to Ce⁴⁺ and Ce³⁺ species [26]. Holgado et al. [27] reported that Ar⁺ bombardment of CeO₂ produces a complete reduction to Ce₂O₃ by preferential removal of oxygen from the altered zone in the XPS measurement process. Sun et al. [28] demonstrated that the banding energy exhibited at ~882 and ~886 eV could be ascribed to CeO₂ and Ce₂O₃. In this literature, the XPS results of Ce3d5 spectra for Ce-Ni₂P/SBA-15 catalysts were consistent well with the publications.

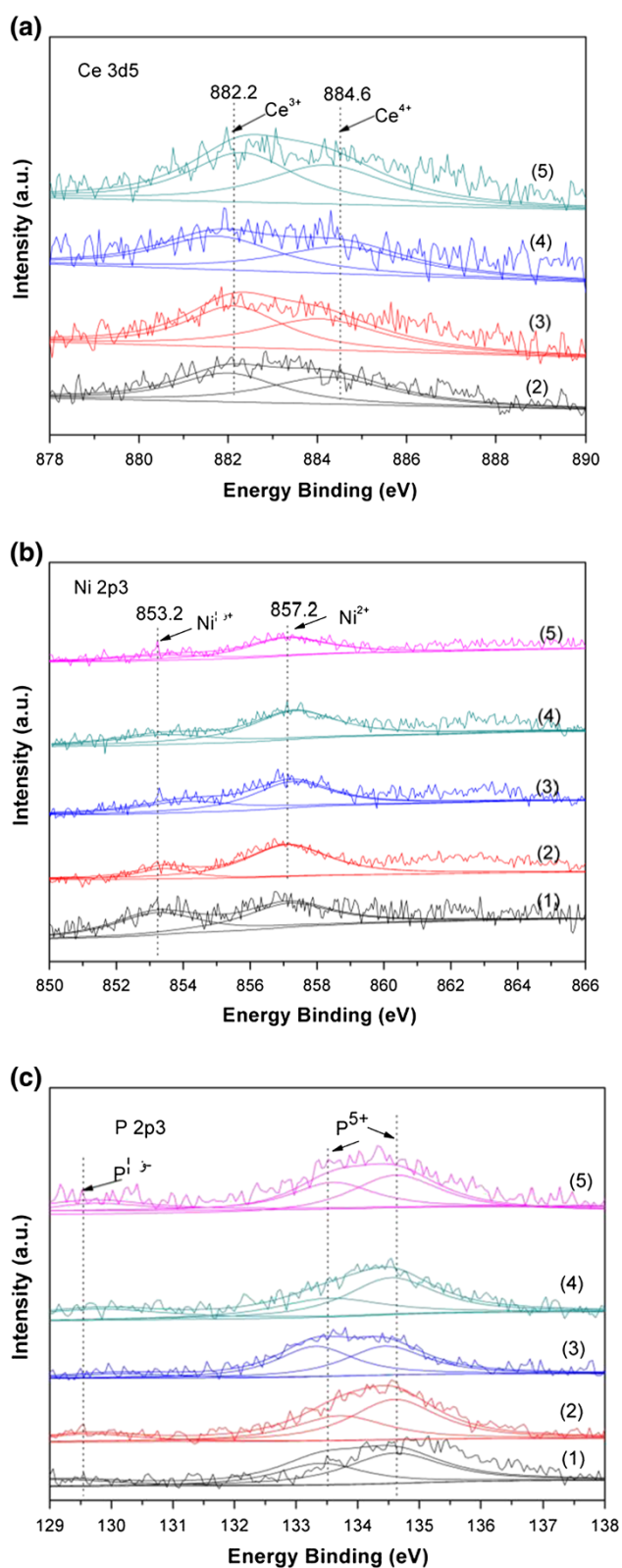


Fig. 4 XPS spectra of Ce-Ni₂P/SBA-15 catalysts with different Ce loadings **a** Ce3d5, **b** Ni2p3, **c** P2p3, 1 Ni₂P/SBA-15, 2 1 % Ce-Ni₂P/SBA-15, 3 3 % Ce-Ni₂P/SBA-15, 4 5 % Ce-Ni₂P/SBA-15, 5 7 % Ce-Ni₂P/SBA-15

Ni2p3 spectra of Ce-Ni₂P/SBA-15 catalysts are present in Fig. 4b. For Ni₂P/SBA-15 catalyst, the Ni2p3 BE peaks were at 853.5 and 857.2 eV, respectively. This could be assigned to Ni^{δ+} ($0 < \delta < 2$) and Ni²⁺. With regard to Ce-Ni₂P/SBA-15 catalysts, the Ni2p3 BE peaks were almost unaffected by the addition of Ce, suggesting that the addition of Ce did not affect the electronic properties of Ni₂P/SBA-15 catalyst. This was probably due to the Ce species introduced by the impregnation method which were mainly located on the surface of the catalysts. It was reported by Burns et al. [29] that the Ni 2p3/2 binding energy at 853.7 and 857.3 eV was assigned to Ni^{δ+} species and Ni²⁺ species. Ni²⁺ species was formed in Ce-Ni₂P/SBA-15 catalysts because the samples were passivated with 1 % O₂ in Ar before XPS measurement.

Figure 4c shows the P2p3 spectra of Ce-Ni₂P/SBA-15 catalysts. In the case of Ni₂P/SBA-15 catalyst, the P2p3 BE peaks located at 129.5 eV could be attributed to P^{δ-} species, and could be related to Ni₂P. The BE peaks located at 133.3 and 134.6 eV could be attributed to P⁵⁺ species, which could be related to phosphate ions and phosphorus pentoxide. For Ce-Ni₂P/SBA-15 catalysts, the value of the BE peaks was also located at the same position. It meant that the addition of Ce in Ni₂P/SBA-15 catalyst did not affect the valence of P. It had been reported that the formation of phosphorus pentoxide is mainly due to the superficial oxidation of nickel phosphide after the passivation by 1 % O₂/Ar (v/v) [29].

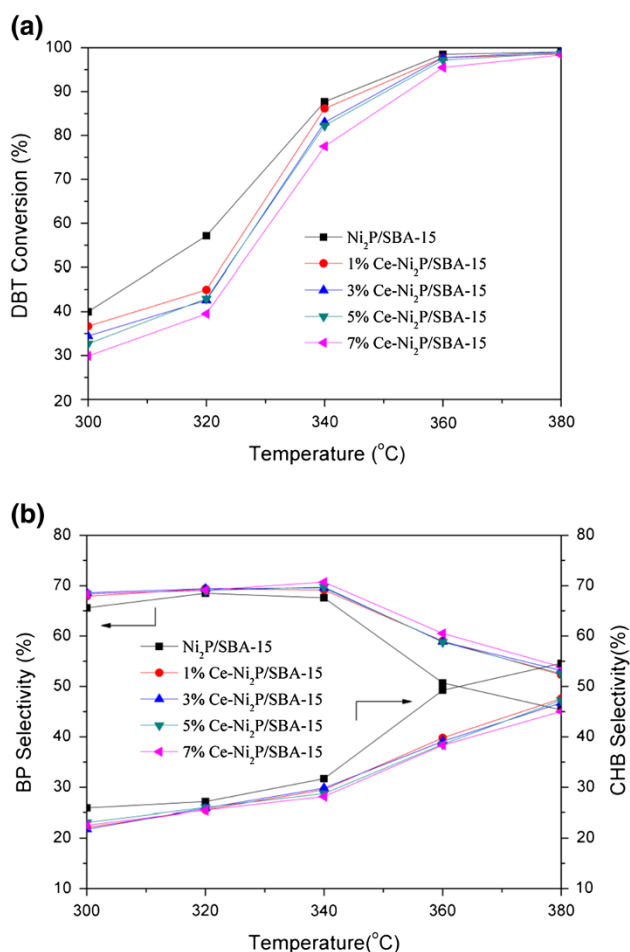
The surface atom concentration and the binding energy are shown in Table 3. As seen in the Table 3, the Ce surface atom concentration increased with the increasing of Ce loadings. Ni^{δ+} atom relative concentration evidently decreased with the increasing of Ce loadings. P atom relative concentration slightly shifted to the low value, indicating that the amount of active sites decreased when Ce was added to Ni₂P/SBA-15 catalyst. Oyama et al. had been reported that Ni^{δ+} in Ni₂P was the active site for HDS of 4,6-DMDBT [10]. So the decreasing of Ni^{δ+} species reduced the activity of DBT HDS over Ce-Ni₂P/SBA-15 catalysts.

Catalytic activity of Ce-Ni₂P/SBA-15 catalysts

The catalytic performance of Ce-Ni₂P/SBA-15 catalysts with different Ce loadings for HDS of DBT is presented in the Fig. 5a. The conversion of DBT was 40.8 % at 300 °C and 98.9 % at 380 °C over Ni₂P/SBA-15 catalyst. Compared with Ni₂P/SBA-15 catalyst, Ce-Ni₂P/SBA-15 catalysts had lower DBT conversion at 300–340 °C, and DBT conversion decreased with the increasing of Ce loadings. This was attributed to the relative concentration of Ni^{δ+} was decreased when Ce was added to Ni₂P/SBA-15 cata-

Table 3 XPS results of Ce-Ni₂P/SBA-15 catalyst with different Ce loadings

Catalysts	Ce 5d3		Ni 2p3		Ni ^{δ+} /Ni	P 2p3			Si 2p		O 1s	
	BE (eV)	At (%)	BE (eV)	At (%)		BE (eV)	At (%)	P ^{δ-} /P (%)	BE (eV)	At (%)	BE (eV)	At (%)
Ni ₂ P/SBA-15	–	–	853.5; 857.2	0.66	0.30	129.5; 133.4; 134.6	2.90	0.14	103.3	27.72	533.2	68.56
1 % Ce-Ni ₂ P/SBA-15	882.2; 884.6	0.25	853.4; 857.2	0.58	0.25	129.4; 133.6; 134.6	4.69	0.15	103.3	27.24	533.0	66.77
3 % Ce-Ni ₂ P/SBA-15	882.2; 884.6	0.35	853.3; 857.1	0.56	0.20	129.6; 133.3; 134.4	4.03	0.14	103.0	25.23	532.5	69.39
5 % Ce-Ni ₂ P/SBA-15	882.1; 884.5	0.39	853.5; 857.2	0.60	0.19	129.4; 133.4; 134.3	3.67	0.15	103.3	28.43	533.0	66.42
7 % Ce-Ni ₂ P/SBA-15	882.1; 884.5	0.51	853.0; 857.2	0.62	0.17	129.5; 133.5; 134.3	4.34	0.10	103.3	25.43	532.8	68.60

**Fig. 5** HDS of DBT over Ce-Ni₂P/SBA-15 catalysts with different Ce loadings **a** activity **b** BP and CHB selectivity

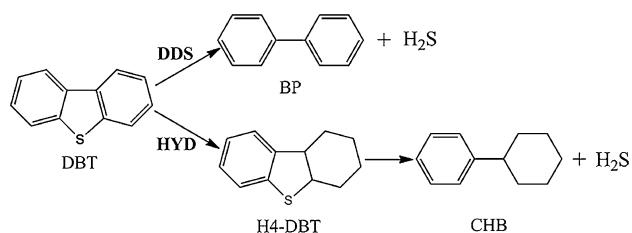
lyst. In other words, the contact of the reactants and the Ni₂P active site may be restrained by adding Ce to Ni₂P/SBA-15 catalyst. 7 % Ce-Ni₂P/SBA-15 catalyst had the lowest DBT conversion at lower temperature, which can reach 29.9 % at 300 °C and 77.5 % at 340 °C.

It can be proposed that not only the low Ni₂P active sites but also the formation of Ni₁₂P₅ resulted in lowest activity over 7 % Ce-Ni₂P/SBA-15 catalyst. Korányi et al. [30] reported that Ni₁₂P₅ gave a lower active when

compared with Ni₂P for HDS of DBT. At 360–380 °C, Ni₂P/SBA-15 and Ce-Ni₂P/SBA-15 catalysts exhibited similar HDS conversion. Chen et al. [31] reported that the apparent reaction rate constant increased with increasing the temperature. Higher DBT conversion was shown over Ni₂P/SBA-15 catalyst than that over Ce-Ni₂P/SBA-15 catalyst at 300–340 °C, mainly due to more active sites in Ni₂P/SBA-15 catalyst. DBT HDS reaction had high apparent reaction rate constant at 360–380 °C. So Ce-Ni₂P/SBA-15 catalyst with fewer active sites exhibited similar DBT conversion with Ni₂P/SBA-15 catalyst.

Furthermore, –OH on the surface of SBA-15 could connect Ce and form Si–O–Ce bond [32, 33], and this bond may block the mouth of the mesopore. This meant that less contents of DBT could come into the pore of Ce-Ni₂P/SBA-15 catalysts, and this could decrease the conversion of DBT. From the data of pore structure parameters and previous reference [20], we could also get this point. Then the contents of Ce reached 7 %. Some of Ce was incorporated into SBA-15 and led to the decrease of surface areas. Then the conversion of DBT could be reduced due to the decreased surface areas. This was also consistent with our previous research [34].

The Fig. 5b shows the selectivity of BP and CHB over Ce-Ni₂P/SBA-15 catalysts with different Ce loadings. BP and CHB selectivity over Ni₂P/SBA-15 catalyst was changed slightly at 300–340 °C, and BP selectivity decreased apparently at 360–380 °C. Compared with Ni₂P/SBA-15, BP and CHB selectivity over Ce-Ni₂P/SBA-15 was similar at 300–340 °C, respectively. However, BP selectivity was apparently lower than that of Ce-Ni₂P/SBA-15 at 360–380 °C. So the addition of Ce to Ni₂P/SBA-15 catalyst could regulate the selectivity of BP and CHB at 360–380 °C. Generally, BP, CHB and traces amount of H4-DBT (can be neglected) are the products of DBT HDS. The mechanism of DBT HDS could occur through two parallel reactions (seen in scheme 1), direct desulfurization (DDS) and desulfurization after hydrogenation (HYD). For DDS route, the main product is BP. For HYD route, H4-DBT is first developed and then



Scheme 1 The mechanism of dibenzothiophene hydrodesulfurization

quickly converted to CHB [35]. Abu et al. [12] reported that the 4,6-DMDBT selectivity can be enhanced by adding Co species to Ni_2P due to the increased acidity. In this paper, the addition of Ce to $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst improved the strength of acid site and the amount of acid. BP selectivity over Ce- $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst was higher than that of $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst especially at 360–380 °C, indicating that increased acid properties could enhance BP selectivity over Ce- $\text{Ni}_2\text{P}/\text{SBA-15}$ catalysts. On the contrary, CHB selectivity was decreased during this period. In other words, the enhanced BP selectivity followed DDS route over Ce- $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst when compared with $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst.

Conclusions

A series of Ce- $\text{Ni}_2\text{P}/\text{SBA-15}$ catalysts with different Ce loadings were prepared by impregnation method. The structure of as-synthesized catalysts and their HDS performance were investigated. Only Ni_2P phase existed in Ce- $\text{Ni}_2\text{P}/\text{SBA-15}$ when $\text{Ce} \leq 5$ wt %, and Ni_2P and Ni_{12}P_5 phases existed in 7 % Ce- $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst. The surface area and pore volume were increased when Ce was added to $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst. The strength of acid site and the amount of acid over Ce- $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst was higher than that over $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst. The amount of active sites in $\text{Ni}_2\text{P}/\text{SBA-15}$ was higher than that of Ce- $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst. Compared with $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst, the Ce- $\text{Ni}_2\text{P}/\text{SBA-15}$ catalysts gave lower HDS of DBT performance at 300–340 °C. However, similar catalytic activity was showed over these catalysts for HDS of DBT at 360–380 °C. The addition of Ce to $\text{Ni}_2\text{P}/\text{SBA-15}$ catalyst apparently enhanced BP selectivity at 360–380 °C.

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