Nickel Phosphide Supported on ZrO$_2$ Modified SBA-15 Dibenzothiophene Hydrodesulfurization Catalysts: Preparation, Characterization and Evaluation

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Abstract
Ni$_3$P/ZrO$_2$-SBA-15 catalysts with different zirconium n-propoxide/SBA-15 mass ratio were synthesized to evaluate their dibenzothiophene hydrodesulfurization catalytic activity. Effect of ZrO$_2$ introduction was investigated. Supports and catalysts were characterized by BET, XRD, $^{29}$Si NMR, XPS and FTIR. The results indicated that zirconium was incorporated into SBA-15 in the form of [(-O-)$_2$Si(-O-Zr)$_2$] and/or [(-O-)$_2$Si-O-Zr], and that the SBA-15 framework structure was still kept intact after incorporation of ZrO$_2$. With zirconium content increasing, ZrO$_2$ is transformed from amorphous phase to tetragonal phase. There might be some kind of interaction occurring between P species and Zr species. Besides Ni$_3$P, another kind of active phase, ZrP, was formed, which might have a better HDS activity than Ni$_3$P. It was observed that with the temperature of 280 °C, the pressure of 3.0 MPa, the WHSV of 6.5 h$^{-1}$ and the H$_2$ to oil ratio of 450, the Ni$_3$P/Zr-SBA (1.5) catalyst, where 1.5 represents zirconium n-propoxide/SBA-15 mass ratio, showed the highest DBT conversion, which was 86.6%, almost 35% percent higher than Ni$_3$P/Zr-SBA(0) catalyst.

Key words: Nickel Phosphide, Zirconium Phosphonate, Hydrodesulfurization, ZrO$_2$ Modified SBA-15.

1. INTRODUCTION
Sulfur content in fuel has been restricted stringently according to environmental requirements. The recent research results indicated that transition metal phosphide has much more surface activity sites for catalytic hydrodesulfurization than sulfide catalysts. Also, phosphide catalysts have better hydrogenation selectivity and less hydrogen consumption (Wang and Ruan, 2005). Therefore, the investigation of transition metal phosphide HDS catalysts has received great attention in recent years. HDS catalytic activity of nickel phosphide is the highest among all the transition metal phosphides (Infantes-Molina and Cecilia, 2010). Mesoporous materials and molecular sieves have a larger specific surface area and a more regular pore structure than conventional γ-Al$_2$O$_3$ supports, and are more suitable for the diffusion and reaction of macromolecules, such as dibenzothiophene, dimethyl dibenzothiophene and 4,6-dimethyl dibenzothiophene (La Parola and Dragoi, 2010). Pure siliceous mesoporous materials are limited in industry due to lack of chemical reaction activity. Some modifications of silica have been developed to increase the metal-support interactions, e.g., ZrO$_2$ or TiO$_2$ grafting of SiO$_2$ (Valencia and Klimova, 2011).

Due to the high HDS catalytic activity of Ni$_3$P and good performance of ZrO$_2$ incorporated into pure siliceous mesoporous material, in this paper, catalysts with different zirconium n-propoxide/SBA-15 mass ratio were synthesized. And dibenzothiophene was used as a model compound to evaluate the hydrodesulfurization performance of the synthesized catalysts on a high pressure micro-fixed-bed reactor.

2. EXPERIMENTAL
2.1 Support and Catalyst Preparation
SBA-15 was synthesized according to the procedure reported in literature (Zhao and Feng, 1998). The triblock copolymer Pluronic P123 (M = 5800, EO$_3$PO$_9$EO$_{30}$ ≥99%, Aldrich) and tetraethyl orthosilicate (TEOS, ≥99%, Jiang Tian Chemical) were used as structure-directing agent and silica source respectively.

ZrO$_2$ modified SBA-15 supports were prepared by chemical grafting method, using zirconium n-propoxide (Zr(n-PrO)$_4$, 70 wt.% in 1-propanol, Aldrich) as zirconia source, and dry ethanol (EtOH, ≥99%, Jiang Tian Chemical) as solvent. In the grafting procedure, dried SBA-15 was slurried in EtOH containing Zr(n-PrO)$_4$ for 24 h at room temperature. To eliminate excess Zr(n-PrO)$_4$, the filtered mixture was washed three times with dry EtOH. The solid was then dried in air at room temperature and calcined in air at 550 °C for 6 h. Hereafter, ZrO$_2$
grafted SBA–15 materials will be denoted as Zr–SBA(x) samples, where x represents mass ratio of zirconium n-propoxide/SBA–15 (x = 0.5, 1.5, 2.5).

The amount of nickel nitrate (Ni(NO₃)₂·6H₂O, ≥98%, Aldrich) and diammonium phosphate ((NH₄)₂HPO₄, ≥98.5%, Aldrich) were calculated according to the mass fraction of Ni₃P in the ZrO₂–SBA–15 support (20%) and the mole ratio of Ni/P (Ni/P = 1/2). The specific amount of Ni(NO₃)₂·6H₂O and (NH₄)₂HPO₄ were added into deionized water, resulting in bright yellow precipitates. Then dilute nitric acid was added drop by drop until the precipitates were completely dissolved to get a dark green solution. The dried Zr–SBA(x) support was impregnated with the prepared solution for 24 h at room temperature. The mixture was then heated at 100 °C for 24 h to evaporate water, and then the obtained solid was calcined in air at 500 °C for 4 h. The precursor finally got were pelleted, crushed and sieved to 40–60 mesh.

A certain amount of 40–60 mesh nickel phosphate precursor particles were placed in a tubular stainless steel reactor, the inner diameter of which was 8 mm. H₂ (99.999%, Air Product) was introduced at a flow rate of 50 ml/min. The temperature was raised from room temperature to 300 °C with heating rate of 10 °C/min, and from 300 °C to 550 °C with heating rate of 1 °C/min, and finally kept constant at 550 °C for 2 h. Then the temperature was lowered down to room temperature in H₂ atmosphere, and was followed by passivation using 1% O₂/N₂ (50 ml/min) for 2 h. Hereafter, prepared Ni₃P/ZrO₂–SBA–15 catalysts will be denoted as Ni₃P/Zr–SBA(x) samples, where x represents mass ratio of zirconium n-propoxide/SBA–15.

2.2 Characterization

Nitrogen adsorption-desorption isotherms were obtained on an Auto-sorb-iQA3200-4 (Quantatech Co., USA) apparatus. Prior to the experiments, the samples were degassed at 270 °C in a vacuum for 6 h. Specific surface area (A_{BET}) was calculated by the BET equation and average pore diameter was calculated by applying the Barret-Joyner-Halenda method (BJH). X-ray diffraction (XRD) patterns were collected with a D/MAX-2500 diffractometer by using Cu Kα radiation. The samples were scanned from 0.5° to 5° with the speed of 0.5 °/min and 10° to 80° with the speed of 8 °/min. The 29Si NMR spectra were obtained under magic angle spinning (MAS) conditions using a Varian Infinityplus 300 spectrometer with a magnetic field strength of 7.0 T, and a sample spinning rate of 4.0 kHz. X-ray photoelectron spectroscopic (XPS) experiments were performed using a Thermo Fisher K-Alpha system. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). FTIR spectra were acquired using a Nicolet-380 Fourier Transform Infrared Spectrophotometer. Measurements were taken from 400 to 4000 cm⁻¹ at a resolution of 8.0 cm⁻¹, and 32 scans were averaged.

2.3 Catalytic Activity Evaluation

HDS reaction was carried out in tubular stainless steel fixed-bed reactor. For a typical reaction, a quantity of 1.5 g precursor was held in the middle of the reactor by two layers of quartz sand. Prior to reaction, the precursor was reduced in a H₂ flow as mentioned above. The HDS performance of the catalyst was evaluated using 1.0 wt.% DBT in cyclohexane (containing 1.0 wt.% n-dodecane as internal standard) as feedstock. The operating conditions were 260–340 °C, 3.0 MPa, WHSV = 6.5 h⁻¹, and a H₂ flow rate of 90 ml/min. The sampling of liquid product was started when reaction conditions had stabilized, and was collected at an interval of 1 h. The first liquid product sample was collected at 260 °C and reaction temperature was raised by 20 °C at an interval of 1 h, finally reaching 340 °C.

Both feed and liquid samples were analyzed by means of an SP7890 gas chromatography equipped with an FID detector using a commercial OV-101 capillary column. In the DBT HDS reaction, only small amounts of sulfur-containing intermediates were detected and therefore conversion of DBT was used to measure HDS performance of the catalysts.

3. RESULTS AND DISCUSSION

3.1 Characterization of SBA–15 and ZrO₂–SBA–15 Supports

The synthesized pure siliceous SBA–15 and SBA–15 with varying zirconia containing, ZrO₂–SBA–15 supports are characterized by X-ray diffraction and N₂ adsorption-desorption isotherms in order to establish the structural and textural properties.

Fig. 1 shows XRD patterns of synthesized pure siliceous SBA–15 and ZrO₂–SBA–15 samples. Both samples exhibit three diffraction peaks in small angle XRD pattern and one diffraction peak in wide angle XRD pattern. Zr–SBA(x) samples show similar patterns as SBA–15, indicating that hexagonal order remains more or less intact after introduction of ZrO₂. No ZrO₂ peak is detected, indicating that amorphous ZrO₂ is formed. In small angle XRD pattern, because of ZrO₂ addition, all the peaks of Zr–SBA(x) samples exhibit minor changes moving to left, which means that planes spacing is becoming larger. In wide angle XRD pattern, the mesoporous SiO₂ typical peak of Zr–SBA(x) samples is slightly wider than pure SBA–15, which means that structural integrity and long-order pore arrangement of SBA–15 has been a little affected with ZrO₂ addition. However, SBA–15 can stand from this kind of mesoporous framework structural destruction.
All the SBA–15 supports with varying ZrO₂ content are examined by BET surface area and BJH adsorption pore size distribution. The N₂ adsorption-desorption isotherms and pore size distribution curves of these four samples are shown in Fig. 2. All these samples exhibit typical type-IV isotherms with hysteresis loop, which correspond to hexagonal pore system, and also exhibit narrow pore size distributions. Textural characteristics of all the samples are listed in Table 1. Incorporation of ZrO₂ has a significant effect on the BET surface area and pore size of the final materials. With ZrO₂ content increasing, the BET area almost remains stable around 480 m²/g, the pore size decreases from 6.38 nm to 6.04 nm, the pore volume decreases to around 0.70 cm³/g.

![Figure 1 Small (1) and wide (2) angleXRD patterns of Zr-SBA(x) supports samples with different x values](image1)

![Figure 2 N₂ adsorption-desorption isotherms (1) and BJH pore size distribution curves (2) of the supports](image2)

### Table 1 Textural characteristics of Zr-SBA(x) supports with varying ZrO₂ content

<table>
<thead>
<tr>
<th>Sample</th>
<th>A_BET/(m²/g)</th>
<th>D_BJH/(nm)</th>
<th>V_p/(cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-SBA(0)</td>
<td>723.32</td>
<td>6.38</td>
<td>1.07</td>
</tr>
<tr>
<td>Zr-SBA(0.5)</td>
<td>625.38</td>
<td>6.02</td>
<td>0.90</td>
</tr>
<tr>
<td>Zr-SBA(1.5)</td>
<td>480.92</td>
<td>6.15</td>
<td>0.70</td>
</tr>
<tr>
<td>Zr-SBA(2.5)</td>
<td>472.60</td>
<td>6.04</td>
<td>0.68</td>
</tr>
</tbody>
</table>

After conforming the prepared supports remain SBA–15 like structural arrays, the location of the Zr centers and their environments was studied by using ²⁹Si MAS NMR.

Fig. 3 compares the ²⁹Si MAS NMR spectra of Zr–SBA(x) with that of pure siliceous SBA–15. In Fig. 3 (1), the ²⁹Si MAS NMR spectrum of the pure siliceous SBA–15 shows a sharp and strong peak in the Q₂(–O–)₄Si region (δ = -110.37 ppm), a shoulder in the Q₃[–O–]₂Si(OH) region (δ = -101.23 ppm) and a small peak in the Q₃[–O–]₂Si(OH)₂ region (δ = -91.45 ppm). Peak area of Q₂ is the smallest, which can be attributed to the preparation process of SBA-15. After SBA-15 was calcined at 550 °C in order to remove the template, the amount of –OH would decrease sharply. Theoretically, peak area of Q₂ is supposed to be smaller than Q₃, and Q₁ is supposed to be smaller than Q₄, which is consistent quite well with the results we obtained. No significant changes in the position of Q₁, Q₂ and Q₃ peaks can be seen in Fig. 3 (2), (3) and (4). However, Q₄ peak is not detected in Fig. 3 (2), (3) and (4). This might because in chemical grafting procedure, reaction activity of [–O–]₂Si(OH)₂ is higher than that of [–O–]₂Si(OH). So [–O–]₂Si(OH)₂ reacted with zirconium n-propoxide firstly to form [–O–]₂Si(–O–Zr)₂. According to the relevant literature(Kenneth and Smith, 2002), also considering that the existence of Q₂ was very unlikely after calcined at 550 °C, the peak appeared at low chemical shifts could be attributed to [–O–]₂Si(–O–Zr)₂. The other wide new peak which was centered at about -110 ppm
could be attributed to \([(-O-)_{2}Si-O-Zr]\). All the above peaks indicate that the zirconium species have been successfully incorporated in to the pure siliceous SBA-15. Interestingly, it can be easily found out that peak area of \([(-O-)_{3}Si-O-Zr]\) in Fig. 3 (3) is the largest among Fig. 3 (2), (3) and (4) and peak area of \([(-O-)_{2}Si(-O-Zr)_{2}]\) in Fig. 3 (2), (3) and (4) are almost equal. So here it is proposed that Zr–SBA(1.5) might be a more preferable support as Zr species were converted to \([(-O-)_{2}Si-O-Zr] and \([(-O-)_{2}Si(-O-Zr)_{2}]\) more completely than Zr–SBA(0.5) and Zr–SBA(2.5). This could be explained by that appropriate amount of ZrO2 incorporation into SBA-15 is essential to get a more complete conversion of \([(-O-)_{2}Si-O-Zr] and \([(-O-)_{2}Si(-O-Zr)_{2}]\), neither too little nor too much.

![Figure 3](image)

**Figure 3** \(^{29}\)Si MAS NMR spectra of Zr–SBA(0) (1); Zr–SBA(0.5) (2); Zr–SBA(1.5) (3) and Zr–SBA(2.5) (4)

### 3.2 Characterization of Ni\(_2\)P/ZrO\(_2\)-SBA-15 Catalysts

XRD patterns for the Ni\(_2\)P/ZrO\(_2\)-SBA (x) catalysts with different x values are shown in Fig. 4. No t-ZrO\(_2\) peak was detected in Fig. 4. (1) and (2), indicating that amorphous ZrO\(_2\) was formed. With more ZrO\(_2\) incorporation, t-ZrO\(_2\) phase was formed and peaks for t-ZrO\(_2\) phase was detected. Also in Fig. 1 (2), XRD patterns of the Zr–SBA (2.5), no peaks for t-ZrO\(_2\) phase was detected but in Fig. 4 (3), obvious peaks for t-ZrO\(_2\) phase was detected. There might be some kind of interaction occurring between Ni\(_2\)P and ZrO\(_2\) phase because the intensity of Ni\(_2\)P peak decreased obviously with ZrO\(_2\) content increasing.

![Figure 4](image)

**Figure 4** XRD patterns of the Ni\(_2\)P/ZrO\(_2\)-SBA (x) catalysts with different x values. (1) x = 0.5; (2) x = 1.5; (3) x = 2.5

The \(N_2\) adsorption-desorption isotherms curves of Ni\(_2\)P/Zr–SBA(x) catalysts are shown in Fig. 5. Textural characteristics of them are given in Table 2. A significant decrease in BET surface area and total pore volume is
observed in Table 2 and Fig. 5 compared with Table 1 and Fig. 2 when Ni₂P and ZrO₂ incorporated into the support. Therefore, it can be deduced that some destruction of the support pores or a partial collapse of its structure might take place in Ni₂P/Zr–SBA(x) catalysts after Ni₂P and ZrO₂ deposition.

![Figure 5](image)

**Figure 5** N₂ adsorption-desorption isotherms of Ni₂P/Zr–SBA(x) catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>(A_{BET} (m^2/g))</th>
<th>(D_{BJS} (nm))</th>
<th>(V_t (cm^3/g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₂P/Zr-SBA(0.5)</td>
<td>342.7</td>
<td>7.62</td>
<td>0.652</td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(1.5)</td>
<td>186.2</td>
<td>6.36</td>
<td>0.296</td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(2.5)</td>
<td>168.6</td>
<td>6.53</td>
<td>0.275</td>
</tr>
</tbody>
</table>

In order to get further information about the surface composition of the catalysts, XPS was employed. Table 3 shows the binding energy values and superficial Ni/P atomic ratios for the catalyst samples.

**Table 3-1** Binding energy of the catalysts obtained by XPS analysis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Binding energy (eV)</th>
<th>Ni 2p</th>
<th>P 2p</th>
<th>Zr 3d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ni₂P</td>
<td>Ni²⁺</td>
<td>Ni₂P</td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(0.5)</td>
<td>852.8</td>
<td>856.4</td>
<td>128.9</td>
<td>135.9</td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(1.5)</td>
<td>853.5</td>
<td>856.9</td>
<td>135.5</td>
<td>138.4</td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(2.5)</td>
<td>852.9</td>
<td>856.3</td>
<td>136.9</td>
<td></td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(0)</td>
<td>854.4</td>
<td>856.2</td>
<td>128.4</td>
<td>135.9</td>
</tr>
</tbody>
</table>

**Table 3-2** Superficial atomic ratio of Ni/P obtained by XPS analysis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Superficial atomic ratio of Ni/P beforeand after HDS reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before</td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(0)</td>
<td>0.100</td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(0.5)</td>
<td>0.100</td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(1.5)</td>
<td>0.097</td>
</tr>
<tr>
<td>Ni₂P/Zr-SBA(2.5)</td>
<td>0.160</td>
</tr>
</tbody>
</table>

XPS spectra of Ni₂P/Zr–SBA(0) was shown in Fig. 6. Ni 2p core level spectrum involves two contributions. The first one centered at 854.4 eV is assigned to Ni²⁺ in Ni₂P phase and the second one is at 856.2 eV, attributed to Ni²⁺ interacting possibly with phosphate ions as a consequence of a superficial passivation, along with the shake-up peak at approximately 6.0 eV above the Ni²⁺ species (Song and Wang, 2014). This satellite is due to divalent species, also in the literature has been ascribed to trivalent and oxysulfided nickel species (Cecilia and Infantes-Molina, 2009). Other broad peaks centered at high binding energy side can be assigned to the Ni 2p signal from oxidized Ni species (Song and Wang, 2014). P 2p core level spectrum involves three contributions. The first one centered at 128.4 eV is assigned to P⁶⁻ in Ni₂P phase and the second one can be assigned to phosphorous derivatives, such as H₂PO₃⁻ and H₃PO₄⁻ (Song and Wang, 2014). The third one centered at 135.9 eV can be attributed to surface metal phosphate species (Cecilia and Infantes-Molina, 2009), due to the superficial oxidation of nickel phosphate bulk particles.
**Figure 6** Ni 2p and P 2p core level spectra for fresh Ni$_2$P/Zr–SBA(0) catalysts

Fig. 7–9 give the Ni 2p, Si 2p, P 2p and Zr 3d core level spectra for Ni$_2$P/Zr–SBA(0.5), Ni$_2$P/Zr–SBA(1.5) and Ni$_2$P/Zr–SBA(2.5) catalysts. Effect of ZrO$_2$ content on the catalysts can be investigated. Si 2p core level spectrum involves two contributions. The first one centered at 103.4 eV is assigned to $\{(-\text{O})_4\text{Si}\}$ (Alexander and Short, 1999) and the second one is at 105.3 eV, which can be attributed to $\{(-\text{O})_3\text{Si(OH)}\}$, $\{(-\text{O})_2\text{Si(-O-Zr)}_2\}$ and/or $\{(-\text{O})_3\text{Si-O-Zr}\}$, because in $^{29}$Si MAS NMR (Fig. 3 (2)–(4)) spectra of Zr–SBA(x) samples, there are three different chemical environments for Si.

**Figure 7** Ni 2p, Si 2p, P 2p and Zr 3d core level spectra for fresh Ni$_2$P/Zr–SBA(0.5) catalysts

These kinds of different chemical environments can cause some little chemical shift for Si (Paparazzo, 1996; Jones and Jiménez-Jiménez, 1997). In Fig. 7, Zr 3d core level spectrum involves three contributions. The first two centered at 183.1 eV and 185.4 eV are assigned to ZrO$_2$ because of multiplet splitting (Galtayries and Sporken, 1998). A new peak centered at 191.4 eV is found, whose binding energy is much higher than the first two which might belong to ZrP (Pan and Zhang, 2007). The layer structured zirconium phosphate (ZrP) can be
intercalated with atoms, molecules, small organic groups and even polymers. The structures and properties of the ZrP intercalation compounds can be deliberately tuned, leading to promising potential applications in many fields (Brunet and Colón, 2015). At the same time, the new P 2p peak signal appearing at a much high binding energy side (higher than 137.0 eV) can be assigned to the P 2p signal from P in ZrP species (Pan and Zhang, 2007). However, the peak intensity of Zr 3d and P 2p of ZrP species in Fig. 8 is the strongest in Fig. 7–9. In Fig. 7, it seems that there is not enough Zr species to react with P species to form ZrP, and in Fig. 9 it seems that Zr species is much too sufficient so that t-ZrO2 is formed, centered at 182.2 eV and 184.5 eV, much lower than 183.1 eV and 185.4 eV because of multiplet splitting in Fig. 7. This can also be proved by XRD analysis above (Fig. 4). It is interesting that appropriate ZrO2 content is necessary to form ZrP phase. The binding energy of Si 2p forming [(-O-)3Si(OH)], [(-O-)2Si(-O-Zr)] and/or [(-O-)Si-O-Zr] in Fig. 8 is much higher than that in Fig. 7 and Fig. 9, this might be due to a stronger interaction of ZrP compound with the material support. At first, this kind of chemical shift was also tried to be attributed to a ZrSiO4 phase, however, this is not logical because if that is true, the binding energy of Zr 3d forming ZrSiO4 would also shift to higher values (Guittet and Crocombette, 2001) and this chemical shift of Zr 3d cannot be found in Fig. 8 compared with Fig. 7 and Fig. 9. So it can be arrived at the conclusion that if ZrO2 content is quite appropriate, ZrP phase can be formed, such as Ni3P/Zr–SBA(1.5) among Ni3P/Zr–SBA(x) catalysts. X = 1.5 might be a more preferable value. Interaction of ZrP compound with the material support is the strongest of all these Ni3P/Zr–SBA(x) catalysts. This is consistent with 29Si NMR analysis of Fig. 3. Zr–SBA(1.5) might be a more preferable support as Zr species were converted to [(-O-)3Si-O-Zr] and [(-O-)2Si(-O-Zr)] more completely than Zr–SBA(0.5) and Zr–SBA(2.5). The reason that no peaks for ZrP phase was shown in XRD pattern might be due to the small crystallite size or a highly dispersion.

**Figure 8** Ni 2p, Si 2p, P 2p and Zr 3d core level spectra for fresh Ni3P/Zr–SBA(1.5) catalysts
Table 3 shows that some of the catalysts don’t show peaks for Ni $2p$ and P $2p$ in Ni$_2$P phase at the same time, so it is doubted that if this phase is indeed formed. However, peaks for Ni$_2$P phase can be observed from XRD in Fig. 4. This could indicate that Ni$_2$P phase is located below a superficial layer of phosphate produced by passivation so that XPS cannot detect. Same explanation is also suitable for P $2p$ and Zr $3d$ in ZrP phase. The theoretical Ni/P ratio corresponding to the precursor materials is 0.5. However, superficial Ni/P ratio of all catalysts in Table 3 is lower than 0.5, which may be due to the enrichment of phosphorous on the surface of the catalysts. An obvious increase in the Ni/P ratio was observed for used Ni$_2$P/Zr–SBA (0) compared with its fresh samples. This may be due to a partial loss of phosphorous due to the formation of volatile P species, such as PH$_3$, during the HDS reaction, leading to a decrease in the amount of P on the surface (Song and Wang, 2014). All the other catalysts show an obvious decrease in the Ni/P ratio after HDS reaction (except Ni$_2$P/Zr–SBA(1.5)). It is proposed that Zr species might react with some of P species to form ZrP resulting in more enrichment of phosphorous on the surface of the catalysts.

The FTIR spectra of Ni$_2$P/Zr–SBA(x) catalyst are shown in Fig. 10. For the Ni$_2$P/Zr–SBA(0) catalyst, stretches at 3404 cm$^{-1}$ and 1620 cm$^{-1}$ are attributed to the stretching vibration and bending vibration of the hydroxyl groups in the adsorbed water or crystalline water molecules. Peaks at 1085 cm$^{-1}$ and the shoulder on the left side of 1085 cm$^{-1}$ belong to the antisymmetric stretching vibration of Si–O–Si bond, and 806 cm$^{-1}$ is the symmetrical stretching vibration peak of Si–O–Si bond (Fu and Zheng, 2015). The peak at 450 cm$^{-1}$ is the bending vibration of Si–O–Si bond; the shoulder on the right side of 1085 cm$^{-1}$ and the peak at 3744 cm$^{-1}$ can be attributed to Si–O–H (Fu and Zhang, 2016). The left shoulder at 450 cm$^{-1}$ can be attributed to the Ni–P bond in Ni$_2$P (Chen and Yang, 2011). All these FTIR characterization results are in accordance quite well with the XRD analysis.

Compared with Ni$_2$P/Zr–SBA(0), intensity of the peak at 3744 cm$^{-1}$ decreases for other ZrO$_2$ modified catalysts, that is, the amount of silanol groups decreases. During the preparation process, zirconium n-propoxide reacted with the –OH groups on the surface of the molecular sieve, forming Si–O–Zr bonds with the Si atoms, which is consistent with the NMR analysis. It is mentioned in the literature that the peak of Si–O–Zr bond is located near 960 cm$^{-1}$, which is close to the peak of Si–O–H bond. After modification by zirconium, the right shoulder peak of 1085 cm$^{-1}$ disappeared, the disappearance does not indicate that no Si–O–Zr bond is formed, the Si–O–Zr peak may be included in the absorption peak at 1085 cm$^{-1}$ (Haskouri and Cabrera, 2002). In addition, a new peak appears at 1396 cm$^{-1}$, which can be attributed to the stretching vibration peak of the P–O–H bond.
this peak can be the characteristic peak of ZrP (Wang and Wu, 2012), together with XPS analysis, it can be concluded that ZrP phase is formed. The peak of Zr–O–P bond stretching vibration is located at about 1063 cm$^{-1}$ (Liu and Liao, 2014), and may be contained in the antisymmetric stretching vibration peak of the Si–O–Si bond at 1085 cm$^{-1}$. With more ZrO$_2$ introduction, the width and intensity of the shoulder on the left side of 450 cm$^{-1}$ is increasing, which could be attributed to Zr–O–Zr bond, which is also mentioned in XRD and XPS part. t-ZrO$_2$ is formed in Ni$_2$P/Zr–SBA(2.5) and amorphous ZrO$_2$ is formed in Ni$_2$P/Zr–SBA(1.5) and Ni$_2$P/Zr–SBA(1.5). Actually, ZrO$_2$ displays up to four bands at 450, 500, 610, and 780 cm$^{-1}$ (Haskouri and Cabrera, 2002).

![Figure 10 FTIR spectra of Ni$_2$P/Zr–SBA(x) catalysts](image)

### 3.3 Catalytic Activity

The DBT HDS performances were evaluated as a function of reaction temperature and shown in Fig. 11. Generally, DBT conversion firstly increases with the reaction temperature, and then decreases. The reaction conversion is affected by both thermodynamics and kinetics. HDS reaction is an exothermic process, with temperature increasing, on one hand, the balance will move towards the endothermic direction, on the other hand, the reaction rate is accelerated. Therefore, there is a preferable reaction temperature for each catalyst.

![Figure 11 DBT conversion as a function of reaction temperature for the Ni$_2$P/Zr–SBA(x) catalysts](image)

Compared with Ni$_2$P/Zr–SBA(0), Ni$_2$P/Zr–SBA(0.5) catalyst shows a rather low activity, this might because some destruction of the support pores or a partial collapse of its structure might take place in Ni$_2$P/Zr–SBA(0.5) catalysts after ZrO$_2$ deposition as mentioned in BET analysis above. With more ZrO$_2$ introduction, the Ni$_2$P/Zr–SBA(1.5) catalyst showed the highest HDS activity, which was 86.6% under 280 °C, almost 35% percent higher than Ni$_2$P/Zr–SBA(0) catalysts. This catalyst shows an excellent low temperature activity. It has been pointed out in XPS analysis that x = 1.5 is a more preferable value for the formation of ZrP, the interaction of ZrP compound with the material support is the strongest of all these Ni$_2$P/Zr–SBA(x) catalysts. So it can be deduced that ZrP phase might have a better HDS performance than Ni$_2$P phase. However, this catalyst is not suitable for a much higher temperature. For the Ni$_2$P/Zr–SBA(2.5) catalyst, as mentioned in characterization part, t-ZrO$_2$ phase was formed. This catalyst shows a better HDS activity than Ni$_2$P/Zr–SBA(0) and Ni$_2$P/Zr–SBA(1.5), especially when the temperature is above 300°C. This is understandable that t-ZrO$_2$ phase is much more stable for a much higher temperature environment than amorphous ZrO$_2$.

### 4. CONCLUSIONS

Ni$_2$P/Zr–SBA(x) catalysts were successfully synthesized. Zirconium was incorporated into SBA–15 in the form of [(–O–)$_2$Si(–O–Zr)$_2$] and/or [(–O–)$_3$Si–O–Zr], and that the SBA–15 framework structure was still kept intact after incorporation of ZrO$_2$. More importantly, there might be some kind of interaction occurring between...
P species and Zr species. Another kind of active phase, ZrP, was formed besides Ni₃P, which might have a better HDS activity than Ni₃P. An intermediate x value is necessary to form ZrP phase. At this condition, the interaction of ZrP compound with the material support is the strongest of all these Ni₃P/ZrSBA(x) catalysts. With the temperature of 280 °C, the pressure of 3.0 MPa, the WHSV of 6.5 h⁻¹ and the H₂ to oil ratio of 450, the Ni₃P/ZrSBA(1.5) catalyst could reach a DBT conversion of 86.6%, almost 35% percent higher than Ni₃P/SBA–15(0) catalyst.

REFERENCES


