Hydrodeoxygenation of methyl palmitate over MCM-41 supported nickel phosphide catalysts

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A B S T R A C T
In this paper, bulk and MCM-41-supported Ni2P catalysts were synthesized by the one-step direct reduction of metal phosphate precursors. The role of cations and anions in the synthesis of Ni2P was studied. Catalytic properties for the hydrodeoxygenation (HDO) of methyl palmitate were first investigated in a continuous-flow fixed-bed microreactor. The resulting catalysts were characterized using XRD, TEM, BET, XPS, and carbon monoxide chemisorption. Results indicated that Ni2P can be synthesized at 600°C from its phosphate precursors with a mole ratio of Ni/P = 2/1. Based on the analytical result of GC-MS, we propose a possible HDO reaction mechanism for the HDO of methyl palmitate on MCM-41-supported nickel phosphide catalysts.

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1. Introduction

The global energy shortage has become an important factor restricting the development of the global economy. In recent times, biomass has attracted much attention as a sustainable resource with advantages over fossil fuels such as renewability, lower expense, a short CO2 cycle, and protection of the environment. Many routes for biomass conversion to liquid transportation fuels have been considered [1]. In the 1980s, first-generation biodiesel was reported, its main component is a fatty acid methyl ester (FAME). Second-generation biodiesel can be obtained by hydrodeoxygenation (HDO) and isomerization of FAME, which is similar to a diesel fuel component and is composed of alkanes [2,3]. To date, most of the attention has been focused on the HDO reactions, mainly involving the cleavage of C–O and C–C bonds [4–7]. In recent years, however, transition metal phosphate catalysts have attracted much attention for HDO [8–12].

In our previous studies, metal phosphate catalysts were synthesized by the thermal decomposition of metal hypophosphate and oxide precursors [13–17]. The oxide precursors were, however, obtained from the calcination of metal phosphate in air in a muffle furnace at 600°C. This step will limit the application of some carrier, such as carbon, which will react with oxygen at high temperatures and waste energy. In this paper, bulk and MCM-41-supported Ni2P catalysts were synthesized by the direct reduction of metal phosphate precursors in one step. The role of cations and anions in the synthesis of metal phosphides also was studied. Compared with the traditional temperature-programmed reduction method [18–20] and direct reduction (DR) method [17], the metal phosphate precursors could be directly reduced in a H2 atmosphere and skip the step of calcination in a muffle furnace at 600°C. Various Ni2P/MCM-41 catalysts were synthesized and tested for the HDO of methyl palmitate, which is a derivative of palm oil and widely distributed in nature. Compared with palmitic acid, methyl palmitate has a lower melting point (30°C), and is more suitable for use in laboratory studies. However, all available reports on the HDO of methyl palmitate describe experiments carried out in a stainless steel batch autoclave reactor [21,22]. We now report on an interesting study of MCM-41-supported nickel phosphide (Ni2P/MCM-41) catalysts for the HDO of methyl palmitate in a fixed-bed microreactor.

2. Experimental methods

MCM-41 was purchased from Tianjin Chem. Sci. Ltd., China. It has a specific surface area of 840.6 m2 g−1, a pore volume of 0.8 cm3 g−1, and a BJH average pore size of 3.3 nm. The other
were of analytical pure grade and purchased from Tianjin Guangfu Fine Chemical Research Institute, China.

2.1. Synthesis of bulk and supported nickel phosphides

The synthesis of nickel phosphide involves two main steps: (1) the metal phosphate precursor is obtained by incipient wetness impregnation, followed by drying, and (2) the phosphate precursor is converted to nickel phosphide in flowing H2. In a typical experiment, bulk nickel phosphide was obtained as follows: Initially, 5.82 g (0.02 mol) Ni(NO3)2·6H2O and 0.98 g (0.01 mol) H3PO4 were dissolved in 20 mL of deionized water and stirred for 1 h. Then, the slurry was evaporated at 120 °C to obtain the precursor. Subsequently, the precursor was reduced to nickel phosphide under flowing H2 (60 mL min⁻¹) at 600 °C for 1 h. Finally, the product was cooled to ambient temperature under flowing H2, and then passivated for 1 h under flowing 1% O2/N2. Similar to the synthesis of bulk nickel phosphide, supported nickel phosphide was prepared by reducing the supported phosphate precursor under flowing H2. In order to evaluate the effects of cations and anions, Ni(NO3)2·6H2O and H3PO4 can be replaced by other salts (such as NiCl2 and Na3PO4).

2.2. Characterization

In our studies, powder X-ray diffraction (XRD) was performed on a Bruker D8 focus diffractometer, with Cu Kα radiation at 40 kV and 40 mA. Transmission electron microscopy (TEM) images were acquired using a Philips Tecnai G2 F-20 field emission gun electron microscope. The Brunauer–Emmett–Teller (BET) specific surface areas were obtained using nitrogen adsorption/desorption measurements at 77 K with a BELSORP-mini instrument. The carbon monoxide (CO) chemisorption was performed with Micromeritics ChemiSorb 2750 gas adsorption equipment. The sample was loaded into a quartz reactor and pretreated in 10% H2/Ar at 450 °C for 3 h. After cooling in He, pulses of 10% CO/He in a He carrier (25 mL min⁻¹) were injected at 30 °C through a loop tube.

2.3. Catalytic activity test

The HDO-catalytic activities were evaluated using 50 wt% methyl palmitate in decalin. The HDO reaction was carried out in a continuous-flow fixed-bed microreactor. The height of the fixed-bed microreactor is 700 mm, which has a constant temperature range of 200 mm. The inner diameter of fixed-bed microreactor is 15 mm. The catalyst was pelleted, crushed, and sieved with 20–40 mesh. Then 2.0 g of catalyst was diluted with SiO2 to a volume of 10.0 mL in the reactor. Prior to the reaction, catalysts were pretreated in situ with flowing H2 (100 mL min⁻¹) for 3 h. The testing conditions for the HDO reaction were 3 MPa, weight hourly space velocity (WHSV) = 3 h⁻¹, and H2/oil = 1000. Liquid products were collected every hour after a stabilization period of 6 h. Both feed and products were analyzed with an Agilent 7890A/5975C GC-MS equipped with a flame ionization detector and an HP-5 column. The methyl palmitate conversion and turnover frequency (TOF) were used to evaluate the HDO activity. The TOF was calculated using Eq. (1):

\[
\text{TOF} = \frac{F_{R_\text{HDO}}}{W \times \text{COuptake}} \times \frac{X_A}{100}
\]

where \(F_{R_\text{HDO}}\) is the molar rate of reactant fed into the reactor (μmol s⁻¹), \(W\) the catalyst weight (g), \(\text{COuptake}\) the uptake of chemisorbed CO (μmol g⁻¹), and \(X_A\) is the reactant conversion (%).

3. Results and discussion

3.1. Synthesis of bulk and supported nickel phosphides

In our previous studies, metal phosphate catalysts were synthesized by the direct reduction of oxide precursors [17], which uses a low H2 flow speed and is not affected by the heating rate. The reduction temperature of the metal phosphate precursors was same as that used in the DR method.

In this paper, the role of cations and anions in the synthesis of nickel phosphides was first studied. Fig. 1 shows the XRD patterns of washed and unwashed samples of nickel phosphides synthesized at 600 °C from NiCl2 and Na3PO4 precursors with a mole ratio of Ni/P = 10/5. Diffraction peaks of Na4P2O7, Ni(OH)2, Na2HPO4, and NaCl (PDF# 5–628) were detected in the unwashed sample. In addition to generating NaCl, sodium ions also generate Na4P2O7, which consumes some of the phosphate. This will lead to the generation of less phosphorus in nickel phosphide. The XRD result of a washed sample proved this; the XRD pattern showed that the sample was a mixture of Ni12P5, Ni5P2, and Ni. In Fig. 2, Na2HPO4 and Na3PO4 were used as the phosphorus sources. Fig. 2 shows the XRD patterns of bulk nickel phosphides synthesized at 600 °C from different precursors with different mole ratios of Ni/P. All the results indicate that the phosphorus content of nickel phosphide increased with a decrease in mole ratio of Ni/P. Compared with Na2HPO4, the effect of Na3PO4 on the synthesis of nickel phosphide was more significant. Fig. 3 shows the XRD patterns of bulk nickel phosphides synthesized at 600 °C from different precursors with a mole ratio of Ni/P = 10/5. The results indicate that Cl⁻, OH⁻, and NO3⁻ had no effect on the synthesis of nickel phosphide. Their similarities are that, at reaction temperature, they can generate volatile substances, which can be removed by the flowing H2. The above results show that the non-volatile cations can affect the generation of nickel phosphide.

Fig. 4 shows the XRD patterns of 15 wt% Ni/P/MCM-41 catalysts synthesized at 600 °C from Ni(NO3)2 and H3PO4 precursors with different mole ratios of Ni/P. We can clearly see that the diffraction peaks of Ni12P5 and Ni5P2 were detected from the precursor.

![Fig. 1. The XRD patterns of washed and unwashed samples synthesized at 600 °C from NiCl2 and Na3PO4 precursors with a mole ratio of Ni/P = 10/5.](image-url)
with mole ratios of Ni/P = 10/5, and 10/8, respectively. The results indicate that, compared with bulk nickel phosphide, the synthesis of supported nickel phosphide requires that the precursor has a slight excess of phosphorus.

Fig. 5 shows the XRD patterns of NiP/MCM-41 catalysts synthesized at 600 °C from Ni(NO₃)₂ and H₃PO₄ precursors with a mole ratio of Ni/P = 10/5, and with different loadings. We can clearly see that the diffraction peaks of Ni₁₂P₅ were detected from the precursor with 10 wt% loading. Under the same mole ratio, diffraction peaks of Ni₂P were detected at 20 wt% loading. The phosphorus content of nickel phosphides increased as the loading increased from 5 to 20 wt%. The result indicates that the synthesis of supported nickel phosphide was affected by loading and mole ratios of Ni/P.

Fig. 6 shows the TEM images of Ni₅P/MCM-41 catalysts synthesized at 600 °C from Ni(NO₃)₂ and H₃PO₄ precursors with a mole ratio of Ni/P = 0/5, and with different loadings: (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, and (d) 20 wt%. The results clearly show that size of the nanoparticles of nickel phosphides increased as the loading increased from 5 to 20 wt%. Increasing the loading will make the active component significantly sintering.

Fig. 7 shows the XPS spectra of 15 wt% Ni₅P/MCM-41 synthesized at 600 °C from Ni(NO₃)₂ and H₃PO₄ precursors with a mole ratio of Ni/P = 10/5. The Ni2p core level spectrum of nickel phosphide involves two peaks. The first one is assigned to Ni⁺⁺⁺ of nickel phosphide and is centered at 852.9 eV. The second one is centered at 857.0 eV, corresponding to Ni²⁺ ions possibly interacting with phosphate ions as a consequence of superficial passivation. Meanwhile, the P2p binding energy of nickel phosphide was observed at 129.4 eV for P⁰⁻ of nickel phosphide and 134.5 eV for surface nickel phosphate species [23]. According to the result in Fig. 5, we can see that Ni₁₂P₅ is the main product for 15 wt% Ni₅P/MCM-41. However, the binding energy of Ni2p at 852.9 eV and P2p at 129.4 eV is not obvious, which may be due to surface of Ni₁₂P₅ is oxidized as a consequence of superficial passivation.

Table 1 shows the physical properties of different samples. Compared with a MCM-41 support, all the catalysts showed a significant
Fig. 6. The TEM images of NiₓP/MCM-41 catalysts synthesized at 600 °C from Ni(NO₃)₂ and H₃PO₄ precursors with a mole ratio of Ni/P = 10/5, and with different loadings: (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, and (d) 20 wt%.

decrease in specific surface area. The specific surface area of the sample decreased with loading amount increased. This is mainly because the increasing loading will lead to obviously sintering of nickel phosphide, which can be seen in the TEM images.

Fig. 7. The XPS spectra of 15 wt% NiₓP/MCM-41 synthesized at 600 °C from Ni(NO₃)₂ and H₃PO₄ precursors with a mole ratio of Ni/P = 10/5.

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_BET (m² g⁻¹)</th>
<th>CO uptakes (µmol g⁻¹)</th>
<th>Conversion (%)</th>
<th>TOF (s⁻¹)</th>
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<td>MCM-41</td>
<td>840.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>5 wt% NiₓP/MCM-41</td>
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<td>10 wt% NiₓP/MCM-41</td>
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<td>84.6</td>
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<tr>
<td>15 wt% NiₓP/MCM-41</td>
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<td>3.1</td>
<td>84.5</td>
<td>0.43</td>
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<tr>
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<td>450.6</td>
<td>2.9</td>
<td>79.7</td>
<td>0.43</td>
</tr>
</tbody>
</table>

3.2. Catalytic activity

The HDO catalytic activities were evaluated using 50 wt% methyl palmitate in decalin. The methyl palmitate conversion, selectivity, and TOF were used to evaluate the HDO activity. Unless otherwise noted, the NiₓP/MCM-41 catalysts were synthesized at 600 °C from Ni(NO₃)₂ and H₃PO₄ precursors with a mole ratio of Ni/P = 10/5. Fig. 8 shows the catalytic activities of 15 wt% NiₓP/MCM-41 before and after activation (testing conditions: 3 MPa, WHSV = 3 h⁻¹, H₂/oil = 1000). The result indicates that the catalyst activity was similar after reduction at 400 °C for 3 h.

Fig. 9 shows the catalytic activities of catalysts at different loadings. The results in Fig. 9a show that the HDO conversion of all the catalysts gradually increased as the reaction temperature increased. The results in Fig. 9b show that the selectivity of pentadecane (C₁₅) and hexadecane (C₁₆) exhibited opposite trends as
the loading increased. As shown in Fig. 5, at the same mole ratio of Ni/P, the phosphorus content of nickel phosphides increased as the loading increased. For Ni₅/P/MCM-41 catalysts, the increasing loading will also lead to obviously sintering of nickel phosphide. The decreased selectivity of C₁₆ may be due to the increasing phosphorus content of nickel phosphides and sintering of nickel phosphide. Table 1 shows the TOFs of Ni₅/P/MCM-41 catalysts with different loadings. The results indicate that they had 2.8, 3.0, 3.1, and 2.9 μmol g⁻¹ CO uptakes; the TOFs at 290 °C were 0.44, 0.44, 0.43, and 0.43 s⁻¹, respectively. The active sites of different catalysts have similar TOF values.

Fig. 10 shows the catalytic activities of catalysts prepared with different mole ratios of Ni/P. As shown in Fig. 10a and b, the HDO conversion and selectivity of C₁₆ gradually decreased with decreasing mole ratios of Ni/P in the precursor. Meanwhile, the amount of C₁₅ gradually increased. Similar to the results in Fig. 9,
the decreased selectivity of C16 may be due to the increasing phosphorus content of nickel phosphides. These results indicate that a decreasing mole ratio of Ni/P in the precursor is unfavorable to the HDO of methyl palmitate.

Fig. 11 shows the catalytic activities of 15 wt% NiP/MCM-41 at different WHSVs (testing conditions: 3 MPa, 290 °C, H2/oil = 1000). It was clearly evident that HDO conversion and selectivity of C16 gradually decreased as the WHSV increased. Meanwhile, the amount of C15 and intermediate state products (such as palmitic acid and hexadecanol) gradually increased.

Fig. 12 shows the catalytic activities of 15 wt% NiP/MCM-41 at different reaction temperatures (testing conditions: 3 MPa, WHSV = 3 h⁻¹, H2/oil = 1000). HDO conversion and selectivity of C15 gradually increased as the reaction temperature increased. Meanwhile, the amounts of C16, palmitic acid, and hexadecanol gradually decreased.

For comparison, we studied the catalytic activities of 15 wt% NiP/MCM-41 and 15 wt% Ni/MCM-41. Fig. 13 shows the catalytic activities of 15 wt% NiP/MCM-41 and 15 wt% Ni/MCM-41 at different reaction temperatures (testing conditions: 3 MPa, WHSV = 3 h⁻¹, H2/oil = 1000). The result indicates that Ni/MCM-41 catalyst having better catalytic activity at low temperatures. However, their catalytic activity becomes similar with increasing reaction temperature. Difference in activity may be due to the different catalyst preparation temperature. High preparation temperature can cause sintering of the catalytic active components. In our studies, 15 wt% NiP/MCM-41 was synthesized at 600 °C, and 15 wt% Ni/MCM-41 was synthesized at 350 °C. Hence, nanoparticle of Ni may have a better dispersion than Ni2P.

We have carried out experiments to get different intermediates by decrease reaction temperature and increase WHSV. However, only palmitic acid and hexadecanol were detected but had a low content. We did not detect other intermediates, such as hexadecan-1-ol, hexadecane, and pentadecene. Based on the above GC-MS results and published similar reports, we propose a possible HDO reaction mechanism of methyl palmitate on MCM-41-supported nickel phosphate catalysts. As shown in Fig. 14, the reaction pathway of the HDO of methyl palmitate involves nine steps. Methyl palmitate could produce hexadecanal by removal of methanol (step 1). Simultaneously, methyl palmitate could produce palmitic acid by hydrogenation followed by methane removal (step 2) [24]. Only one path to produce hexadecanol, which is obtained by hydrogenation of hexadecanal (step 3) [25]. Hexadecanal could produce hexadecene by dehydration (step 4), and hexadecane could be generated from hexadecene by a hydrogenation (step 5) [26]. Palmitic acid could directly generate pentadecane by a decarbonation (step 9) [21]; it could also generate hexadecane by dehydration (step 6) [6,27]. Hexadecanal could directly generate pentadecane by removal of CO (step 7) [28], which could then be hydrogenated to produce pentadecane (step 8). It is worth noting that palmitic acid and hexadecanol were detected but had a very low content (<1.5%), due to high catalytic activity.
4. Conclusions

In summary, bulk and MCM-41-supported Ni2P catalysts were synthesized by the direct reduction of metal phosphate precursors in one step. The XRD results indicate that Ni2P can be synthesized at 600 °C from its phosphate precursors with a mole ratio of Ni/P = 2/1. The synthesis of supported nickel phosphide, compared with bulk nickel phosphide, requires the precursor to have a slight excess of phosphorus. The role of cations and anions in the synthesis of Ni2P was studied. The results indicate that Cl⁻, OH⁻, and NO₃⁻ had no effect on the synthesis of nickel phosphide. Their similarities are that, at reaction temperature, they can generate volatile substances, which can be removed by the flowing H₂. The non-volatile cations (Na⁺) can affect the generation of nickel phosphide. The catalytic properties of the HDO of methyl palmitate were first investigated in a continuous-flow fixed-bed microreactor. The results of the HDO indicate that MCM-41-supported nickel phosphide catalysts exhibited excellent activities. Finally, based on the analytical results of GC-MS, we propose a possible HDO reaction mechanism for the HDO of methyl palmitate on MCM-41-supported nickel phosphide catalysts.

Acknowledgments

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