Kinetic Study of Hydrodeoxygenation of Cresols over Ni₃P and Ce-promoted Ni₃P

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Abstract: Ce is a promising promoter for the unsupported Ni₃P in the HDO of cresols. XRD and XPS results reveal that Ce species in Ce-Ni₃P(0.3) (0.3 = nCe/nNi) were mainly in CePO₄ form and both Ce³⁺ and Ce⁴⁺ coexisted on the surface of the catalysts. Less electron transferred from Ni to P atoms after introducing Ce, which resulted in the enhancement of metallicity of nickel atoms of Ce-Ni₃P(0.3), leading to higher HDO activity. After introduction of Ce, the reaction rate constant increased but the activation energy decreased.

Keywords: Cresol, Hydrodeoxygenation, Kinetic study.

1. Introduction

Bio-oils produced by pyrolysis or liquefaction of lignocellulosic biomass are promising alternative sources for the production of fuels, having a high oxygen content (45-50 wt.%)¹, which leads to undesired properties such as high viscosity, low thermal stability, low heating value and immiscibility with petroleum fractions. Mo- or W-based sulfide catalysts suffer from progressive deactivation during hydrodeoxygenation (HDO) of bio-oils, due to the loss of sulfur in the catalytic phase. As a result, it is necessary to explore non-sulfide catalysts to upgrade bio-oils. In our previous study, we found that Ni₃P and Ce-Ni₃P catalysts presented high activity in the HDO of phenols both in aqueous and oil phase. Hence, the kinetic study of HDO of cresols (including o-cresol, m-cresol and p-cresol) was explored, discussing the reaction pathway and rate-limiting step, in order to develop new catalytic system and design optimal reactor.

2. Experimental

The catalysts were prepared from the oxide precursor by in situ H₂ temperature programmed reduction (TPR) method². The XRD patterns of the catalysts were measured on a Rigaku D/MAX 2400 diffractometer with nickel-filtered Cu-Kα radiation at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) spectra were obtained with a Multilab 2000 X-ray photoelectron spectroscopy spectrometer, using an Mg-Kα source. Transmission electron microscopy (TEM) was measured on a Tecnai G2 F30 transmission microscope operated at 300 kV. The samples for TEM examination were prepared by depositing a drop of an ultrasonic treated ethanol suspension of the solid material onto a carbon-coated Cu grid. Prior to HDO reaction, the precursor was transformed into metal phosphide by in situ H₂ TPR. Afterwards, the reactor was cooled to the reaction temperature, with the total pressure of 4 MPa H₂ (ambient temperature).

3. Results and discussion

As seen in Figure 1a, both samples showed a typical crystalline pattern of Ni₃P. Also, for Ce-Ni₃P(0.3) catalyst, the peaks at 2θ=20, 28.4, 31.4, and 41.6° were attributed to the (101), (111), (102), and (211) planes of CePO₄. It was worth noting that after introduction of Ce, the Ni₃P peaks became more broadened and less intense. TEM images of Ni₃P and Ce-Ni₃P(0.3) catalysts were shown in Figure 1b. Compared with the bulk Ni₃P (Dc = 85.8 nm) catalyst, Ce-Ni₃P(0.3) (Dc = 18.7 nm) had smaller and more uniform Ni₃P particles, indicating that the introduction of Ce decreased the crystallite size of Ni₃P (as seen in Figure 1d). The XPS spectra of the catalysts in the binding energy regions of Ni 2p and P 2p are illustrated in Figure 1c. The peaks at about 852.0 and 129.2 eV are related to the reduced Ni³⁺ (0<δ<2) and P⁶⁺ (0<δ<1), respectively. After introduction of Ce, the binding energy ascribed to Ni³⁺ decreased from 852.0 eV to 851.1 eV, while that of P⁶⁺ increased from 129.2 eV to 129.5 eV. They are evidence for less transfer of electron density from Ni to P atoms after introducing Ce, which corresponds to the enhancement of metallicity of nickel atoms of Ce-Ni₃P(0.3). The sub-bands labeled u and v represent the 3d10⁴f⁰ initial electronic state corresponding to Ce³⁺, while those labeled u’ and v’ represent the 3d10⁴f⁰ initial electronic state corresponding to Ce⁴⁺. The coexistence of Ce³⁺ and Ce⁴⁺ might generate oxygen vacancy by electron transfer, which might contribute the high adsorption capacity of oxygen-containing compounds and high deoxygenation activity.
According to the calculated $k$ and $E_a$ of cresols over these two catalysts summarized in Table 1, it could be concluded as follows: (1) Over these two catalysts, the reactivity of cresols increased with increasing temperature, and Ce-Ni$_3$P(0.3) possessed higher activity than those over Ni$_3$P under the same reaction conditions. After introduction of Ce, the HDO activity of cresols increased, ascribing to the electronic and dispersion effect. (2) Over Ni$_3$P, the activity of cresols decreased as followed: m-cresol > p-cresol > o-cresol. However, over Ce-Ni$_3$P(0.3), p-cresol presented the highest reactivity, followed by m-cresol, with o-cresol the lowest. The different trend of cresol isomers reactivity over these two catalysts might be due to the steric hindrance of methyl group and/or the adsorption characteristic of the reactants.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>reactant</th>
<th>$k$ (mol·g$^{-1}$·min$^{-1}$) $^{[a]}$</th>
<th>$E_a$ (kJ·mol$^{-1}$) $^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$P</td>
<td>o-cresol</td>
<td>0.3</td>
<td>80.8</td>
</tr>
<tr>
<td></td>
<td>m-cresol</td>
<td>0.8</td>
<td>46.2</td>
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<tr>
<td></td>
<td>p-cresol</td>
<td>0.6</td>
<td>52.7</td>
</tr>
<tr>
<td></td>
<td>o-cresol</td>
<td>1.3</td>
<td>57.3</td>
</tr>
<tr>
<td>Ce-Ni$_3$P(0.3)</td>
<td>m-cresol</td>
<td>1.8</td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td>p-cresol</td>
<td>3.4</td>
<td>29.7</td>
</tr>
</tbody>
</table>

[a] Calculated by pseudo first order equation. $k = [\ln(1 - x)]/\tau$, where $x$ and $\tau$ represent the conversion of cresol and weight time, respectively. Weight time ($\tau$) is defined as: $\tau = w_{cat}/n_{feed}$, where $w_{cat}$ and $n_{feed}$ denote the catalyst weight (0.05 g) and the total mole flow rate of the feed, respectively.

[b] The activation energy ($E_a$) is calculated according to Arrhenius equation.

4. Conclusions

Ce is a promising promoter for HDO of cresol over unsupported Ni$_3$P. XRD and XPS results revealed that Ce species in Ce-Ni$_3$P(0.3) were mainly in CePO$_4$ form and both Ce$^{4+}$ and Ce$^{3+}$ coexisted on the surface of the catalysts. Less electron transferred from Ni to P atom after introducing Ce, which corresponded to the enhancement of metallicity of nickel atom of Ce-Ni$_3$P(0.3), leading to higher hydrogenation activity. After introducing Ce, the reaction rate constant increased, but the apparent activation energy decreased. Over Ni$_3$P, the activity of cresols decreased as followed: m-cresol > p-cresol > o-cresol. However, over Ce-Ni$_3$P(0.3), p-cresol presented the highest reactivity, followed by m-cresol, with o-cresol the lowest.

References