Kinetic Study of Hydrodeoxygenation of Cresols over Ni_3P and Ce-promoted Ni_3P

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Abstract: Ce is a promising promoter for the unsupported Ni_3P in the HDO of cresol. XRD and XPS results reveal that Ce species in Ce-Ni_3P(0.3) (0.3 = n_{Ce}/n_{Ni}) 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 atoms after introducing Ce, which resulted in the enhancement of metallicity of nickel atoms of Ce-Ni_3P(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 Ni_3P and Ce-Ni_3P 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* H_2 temperature programmed reduction (TPR) method[2]. 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 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* H_2 TPR. Afterwards, the reactor was cooled to the reaction temperature, with the total pressure of 4 MPa H_2 (ambient temperature).

3. Results and discussion

As seen in Figure 1a, both samples showed a typical crystalline pattern of Ni_3P. Also, for Ce-Ni_3P(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 $CePO_4$. It was worth noting that after introduction of Ce, the Ni_3P peaks became more broadened and less intense. TEM images of Ni_3P and Ce-Ni_3P(0.3) catalysts were shown in Figure 1b. Compared with the bulk Ni_3P (D_C = 85.8 nm) catalyst, Ce-Ni_3P(0.3) (D_C = 18.7 nm) had smaller and more uniform Ni_3P particles, indicating that the introduction of Ce deceased the crystallite size of Ni_3P (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 $Ni^{\delta+}$ ($0<\delta<2$) and $P^{\delta-}$ ($0<\delta<1$), respectively. After introduction of Ce, the binding energy ascribed to $Ni^{\delta+}$ decreased from 852.0 eV to 851.1 eV, while that of $P^{\delta-}$ 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-Ni_3P(0.3). The sub-bands labeled u and v represent the $3d^{10}4f^1$ initial electronic state corresponding to Ce^{3+}, while those labeled u' and v' represent the $3d^{10}4f^0$ initial electronic state corresponding to Ce^{4+}. The coexistence of Ce^{3+} and Ce^{4+} might generate oxygen vacancy by electron transfer, which might contribute the high adsorption capacity of oxygen-containing compounds and high deoxygenation activity.

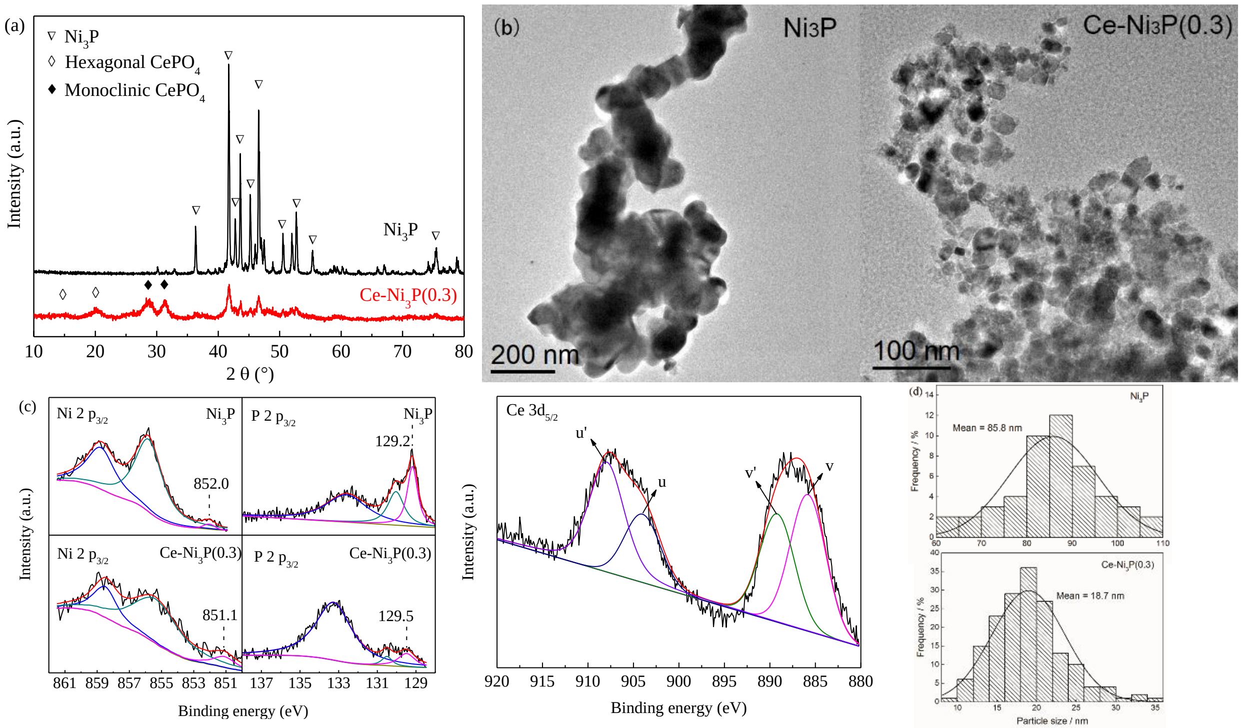

Figure 1. (a) XRD patterns, (b) TEM images, (c) XPS spectra and (d) Particle size distribution of Ni_3P and Ce-Ni_3P(0.3).

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_3P(0.3) possessed higher activity than those over Ni_3P 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_3P, the activity of cresols decreased as followed: m-cresol > p-cresol > o-cresol. However, over Ce-Ni_3P(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 1. HDO of cresols over Ni_3P and Ce-Ni_3P(0.3).

catalyst	reactant	k (mol g^{-1} min^{-1}) [a]				E_a (kJ mol^{-1}) [b]
		150 ℃	175 ℃	200 ℃	225 ℃	
Ni_3P	o-cresol	0.3	1.1	3.9	7.8	80.8
	m-cresol	0.8	1.4	3.2	5.2	46.2
	p-cresol	0.6	1.3	3.0	5.9	52.7
Ce-Ni_3P(0.3)	o-cresol	1.3	2.7	6.8	14.1	57.3
	m-cresol	1.8	3.6	6.8	10.3	41.0
	p-cresol	3.4	4.8	7.2	12.2	29.7

[a] Calculated by pseudo first order equation. $k = [\ln(1-x)]/\tau$, where x and τ represent the conversion of cresol and weight time, respectively. Weight time (τ) 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_3P. XRD and XPS results revealed that Ce species in Ce-Ni_3P(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_3P(0.3), leading to higher hydrogenation activity. After introducing Ce, the reaction rate constant increased, but the apparent activation energy decreased. Over Ni_3P, the activity of cresols decreased as followed: m-cresol > p-cresol > o-cresol. However, over Ce-Ni_3P(0.3), p-cresol presented the highest reactivity, followed by m-cresol, with o-cresol the lowest.

References

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