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Selective Conversion of Phenol in a Subcritical Water Medium Using γ -Al₂O₃ Supported Ni–Co Bimetallic Catalyst

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Abstract: The selective conversion of phenolic materials is a well-adopted solution to upgrade lignin-based bioresources into high-value bio-oil in biomass refinery industries. This study focused on four main aspects: characterization, selection of catalysts, reaction dynamics behaviors, and mathematical modelling. A model lignin, that is, phenol, was selectively transformed into cyclohexanol by using the prepared Ni–xCo/ γ -Al₂O₃ catalysts in a subcritical water medium. The hydrogenation results showed that when using 15 wt% of Ni–3Co/ γ -Al₂O₃ particles, both total mole yield and selectivity of cyclohexanol could reach approximately 80%, which further indicated that the particles are suitable for catalytic hydrogenation of phenol in subcritical water. Moreover, a reaction kinetics model was developed by chemical reaction kinetics and least squares regression analysis, the robustness and predictability of which were also verified.

Keywords: phenol; bio-oil; conversion; subcritical water; NiCo/y-Al₂O₃ catalyst; bimetallic

1. Introduction

At present, the traditional fossil energy crisis and corresponding environmental pollution issues have driven many researchers to develop alternative cleaner energy, such as wind energy, solar energy, hydro energy, biomass energy, etc. [1,2]. Among these sustainable energies, biomass energy (i.e., bioenergy) has already become the fourth-largest global energy source, next only to coal, oil, and natural gas [3]. In recent years, the bioenergy preparation technologies have attracted a great deal of attention across the world, due to the advantages of bioenergy such as low NO₂ and SO₂ emissions as well as zero net carbon emissions [4]. It is known that bioenergy can be directly generated from biomass by hydrothermal liquefaction, pyrolysis gasification, etc. Especially owing to the lower oxygen content and higher calorific value of the produced energy, hydrothermal liquefaction under different conditions (e.g., conventional hydrothermal, supercritical and subcritical fluid, etc.) exhibits incredible potential for direct treatment of wet biomass in its natural state, which can avoid extra energy consumption for drying biomass before pyrolysis processes [5,6].

As the feedstock, the biomass—also called lignocellulosic biomass—is most often comprised of plant materials that are not used for food or feed, the main chemical constituents of which



includes cellulose, lignin, and hemicellulose. Different from the other two mentioned kinds of polysaccharides, as the second most abundant biopolymer, lignin is a class of complex cross-linked phenolic polymers which are mostly driven from three forms of phenylpropanoids: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively, as shown in Figure 1a [7]. Moreover, the bonding types between the lignin units are very complex, which includes β -O-4 linkage, β -5 linkage, β - β linkage, 4-O-5 linkage, 5-5 linkage, β -1 linkage, etc., as seen in Figure 1b [8]. Thus, it is difficult to directly analyze the reaction mechanism of the polymerized lignin. In order to clarify the main hydrothermal liquefaction mechanism, phenol is usually chosen as a normal model compound to represent the three phenylpropanes mentioned above [9–12]. Therefore, in this study phenol was used as a model of lignin for analysis of the selective conversion during the production of phenolic bio-oils.



Figure 1. (a) Structures of three typical monomers of lignin and (b) their bonding types.

During the hydrothermal liquefaction of phenolic materials, catalytic hydrotreatment is a promising technique that can ensure high hydrogenation efficiency under relatively mild conditions, which involves the treatment of raw materials with hydrogen in the presence of heterogeneous catalysts [11]. Noble-metal catalysts (e.g., Ru-, Pt-, and Pd-based catalysts, etc.) exhibit good catalytic efficiency, and have often been used in the corresponding research [12]. However, the high cost of these catalysts greatly limits their industrial applications, which also drives researchers to find alternative metal-based catalysts (e.g., Ni-, Cu-, and Co-based, etc.) [13–15]. Owing to the low cost and high availability, Ni-based catalysts have attracted attention. In order to improve the activity and stability of Ni catalysts, incorporation with other noble metals such as Ru, Pd, Pt, and non-precious metals such as Fe, Co, Zn, Cu, etc. has been investigated [16–18]. Moreover, to improve the catalytic efficiency of these metal catalysts, complete dispersity of catalytic active sites is also required and can be achieved

by coating onto the surface of porous supports, such as MOFs, CeO₂, carbon nitride, carbon, and Al₂O₃ [19–23].

In this study, the Al₂O₃-supported Ni–Co bimetallic catalysts were synthesized by a sequential impregnation method for the catalytic hydrogenation of phenol in a subcritical water medium. The effects of catalyst Ni/Co ratio, reaction time, and temperature on the hydrogenation rate were investigated in this study. The kinetic mechanism of the selective conversion of phenol was also established. Finally, the characteristics of all catalysts were determined by different analytical instruments, such as BET, XRD, XPS, and TEM. The main purpose of this study was to clarify the hydrogenation mechanism of phenolic bio-oil in subcritical water medium, which can provide valuable information for the conversion and utilization of bio-oil to high-grade chemicals.

2. Results and Discussion

2.1. Catalyst Characterization

The structures of the prepared Ni–Co/ γ -Al₂O₃ catalysts were examined by XRD in order to understand their crystal characteristics. As shown in Figure 2, the typical peaks were observed at 32.78°, 36.74°, 39.49°, 45.79°, and 66.98°, which indicated the characteristic peaks of (220), (311), (222), (400), and (440) planes of γ -Al₂O₃, according to the PDF#86-1410 and PDF#98-000-0059 card of XRD. In addition, the XRD diffraction results could also prove the existence of two kinds of spinel NiAl₂O₄ and CoAl₂O₄, which verified the interaction between Ni/Co and γ -Al₂O₃. According to the diagram, the intensity of the diffraction peaks of bimetallic NiCo decreased with the addition of Co, which suggested that the introduction of Co would lead to the better dispersibility of NiCo/ γ -Al₂O₃ catalysts. A similar behavior was reported using monometallic Co into Ni/CNT formation bimetallic catalysts for the hydrodeoxygenation of guaiacol [24].



Figure 2. XRD patterns of (**a**) *γ*-Al₂O₃, (**b**) Ni/*γ*-Al₂O₃, (**c**) Ni-3Co/*γ*-Al₂O₃, (**d**) Ni-1.5Co/*γ*-Al₂O₃, (**e**) Ni-1Co/*γ*-Al₂O₃, (**f**) Ni-0.67Co/*γ*-Al₂O₃, (**g**) Ni-0.33Co/*γ*-Al₂O₃ and (**h**) Co/*γ*-Al₂O₃.

In order to investigate the surface properties of Ni–Co/Al₂O₃ catalysts, the BET-N₂ instrument was employed in this study. The specific surface area, pore volume, and average pore diameter of all catalysts are listed in Table 1. It can be seen that the specific surface area, pore volume, and average pore diameter of the pure γ -Al₂O₃ were 122.75 m².g⁻¹, 0.6627 cm³.g⁻¹, and 22.90 nm, respectively. Moreover, with the increased loading of catalytic active sites, a rapid decrease of the specific surface area, pore volume, and average pore diameter of all supported catalysts were observed (Table 1),

which should be attributed to the destruction of the pore structure during supporting 15 wt% Ni–xCo with γ -Al₂O₃ [25].

	Sample	$\mathrm{S}_{\mathrm{BET}}$ (m ² .g ⁻¹) ^a	V_P (cm ³ .g ⁻¹) ^b	D _P (nm) ^c	
	γ-Al ₂ O ₃	122.75	0.6627	22.90	
N	i/γ -Al ₂ O ₃	109.50	0.5237	17.24	
Ni–3	$3Co/\gamma$ -Al ₂ O ₃	102.48	0.4496	13.76	
Ni-1.	$.5Co/\gamma-Al_2O_3$	113.18	0.4634	13.89	
Ni-1	ICo/γ -Al ₂ O ₃	107.70	0.4922	15.39	
Ni-0.6	67Co/γ-Al ₂ O ₃	105.30	0.5026	16.72	
Ni-0.3	$33Co/\gamma-Al_2O_3$	101.06	0.5149	17.52	
C	o/γ-Al ₂ O ₃	106.42	0.5061	16.28	

Table 1. BET surface area, pore volume, and pore diameter.

Notes: ^a BET surface area. ^b pore volume. ^c average pore diameter.

Moreover, the surface element composition was carried out using XPS. The 15 wt%Ni/ γ -Al₂O₃, 15 wt%Co/ γ -Al₂O₃ and 15 wt%Ni–3Co/ γ -Al₂O₃ catalysts were characterized by XPS. The XPS spectra of Ni 2p and Co 2p are shown in Figure 3A,B. As illustrated, the binding energy of Ni 2p3/2 peak (shown in Figure 3A) was decreased by doping the Co into pure Ni nanoparticles. The decrease of the observed shift in the binding energy verified that the electronic properties of Ni metal were modified with the doping of the second metal. The binding energy of the Co 2p peak was also changed, as shown in Figure 3B, which further confirmed the existence of an intimate interaction between Ni and Co in the Ni–Co alloy [26,27]. The Ni 2p and Co 2p XPS spectra of 15 wt%Ni–3Co/ γ -Al₂O₃ catalysts are shown in Figure 3A,B. Figure 3A shows that the binding energies of 15 wt%Ni–3Co/ γ -Al₂O₃ catalysts were at 855.3 and 861.3eV, which correspond to Ni⁰(2p3/2) and Ni²⁺(2p3/2), respectively. The binding energies at 872.92 and 879.49 eV were attributed to the main line of Ni⁰(2p1/2) and Ni²⁺(2p1/2), which proved the presence of both metallic Ni and NiO on the surface of the support. In Figure 3B, binding energies at 772.92 and 780.45 eV corresponded to Co⁰(2p3/2) and Co²⁺(2p3/2) respectively, and binding energies at 795.99 and 802.92 eV were attributed to the main line of Co⁰(2p1/2) and Co²⁺(2p1/2), which indicated the presence of both metallic Co and CoO [28].



Figure 3. Cont.



Figure 3. XPS spectra of Ni2p region (i.e., **A**) and Co2p region (i.e., **B**) for 15 wt%Ni/ γ -Al₂O₃, 15 wt%Ni-3Co/ γ -Al₂O₃ and 15 wt%Co/ γ -Al₂O₃.

To directly observe the micromorphology of the prepared NiCo-based catalysts, TEM was employed in this study. As can be seen in Figure 4, compared with the 15 wt%Ni/ γ -Al₂O₃ (Figure 4A,B) and the 15 wt%Co/ γ -Al₂O₃ (Figure 4E,F), the 15 wt%Ni-3Co/ γ -Al₂O₃ catalysts (Figure 4C,D) had higher dispersibility and smaller particle size, which indicates that there was a stronger interaction between Ni and/or Co with γ -Al₂O₃ support [29].



Figure 4. Cont.



Figure 4. TEM images of (A,B) 15 wt%Ni/ γ -Al₂O₃, (C,D) 15 wt%Ni-3Co/ γ -Al₂O₃, and (E,F) 15 wt%Co/ γ -Al₂O₃.

2.2. Selection of Catalyst for the Conversion of Phenol

The physicochemical properties of γ -Al₂O₃-supported Ni–Co bimetallic catalysts were also characterized. The results demonstrated that the Ni–Co/ γ -Al₂O₃ catalysts with the different Co loading amounts had different physicochemical properties (e.g., particle size, specific surface area, dispersibility, etc.), which should further affect their catalytic activities. To obtain optimum catalytic efficiency, the prepared catalysts were screened by investigating the conversion process of phenol. During selection, the reaction conditions were fixed as follows: the reaction temperature was 250 °C, the time was 4 h, phenol amount was 2 wt%, water density was 0.1633 g/L, the mass ratio between catalyst and phenol was 1 g/g. As shown in Figure 5, the screen results showed that the 15 wt%Ni-3Co/ γ -Al₂O₃ particles' catalytic activity was obviously the best among these prepared catalysts, with the phenol conversion (i.e., yield) of 82.36%. From Figure 5, it can also be easily seen that with increasing loading ratio of Co, the selective conversion of phenol into cyclohexanol was enhanced. Simultaneously, with increasing loading ratio of Ni, the selective conversion for generating cyclohexanone was also improved. The outstanding catalytic activity (i.e., conversion and selectivity) of bimetallic catalysts may be caused by the unique surface properties of bimetallic alloy nanoparticles. The alloying of Ni and the second metal (i.e., Co) may lead to the change of the catalyst surface by changing the electronic structure of Ni [30,31]. Thus, according to the filtering results, the 15 wt%Ni–3Co/ γ -Al₂O₃ particles were chosen for the analysis of the selective conversion kinetic behaviors of phenol into cyclohexanol in the rest of the study.



Figure 5. Phenol conversion and product selectivity over different catalysts: (**A**) Ni/ γ -Al₂O₃, (**B**) Ni-3Co/ γ -Al₂O₃, (**C**) Ni-1.5Co/ γ -Al₂O₃, (**D**) Ni-1Co/ γ -Al₂O₃, (**E**) Ni-0.67Co/ γ -Al₂O₃, (**F**) Ni-0.33Co/ γ -Al₂O₃, and (**G**) Co/ γ -Al₂O₃.

2.3. Selective Conversion Kinetic Behaviors of Phenol

The 15 wt%Ni–3Co/ γ -Al₂O₃ catalyst was used in the selective conversion of a lignin model (i.e., phenol). The key factors influencing the hydrogenation rate were also investigated (i.e., reaction time and temperature), as seen in Figure 6. Except for time and temperature, other reaction conditions (e.g., water density, phenol amount, the mass ratio between catalyst and phenol catalyst loading, etc.) were fixed similarly as mentioned in the selection of catalyst preparation. As shown in Figure 6, the kinetic results indicated that the conversion yield of phenol increased with the increase of reaction time and temperature, and the products were cyclohexanol (the most important product), benzene, cyclohexanone, and cyclohexane. According to Figure 6, it can be also found that after reaching reaction equilibrium, all of the conversion yields of phenol reached more than 80% at different temperatures. According to Huelsman's study [32], using carbon-supported Rh, Ni, Mo-Ni catalysts or a commercial sulfided NiMo/Al₂O₃ catalyst can only achieve less than 75% conversion of phenol at 310 °C for 120 min with the H₂ pressure of 3 MPa. Thus, it can be concluded that the prepared NiCo-based catalysts in this study are promising for the selective hydrogenation of phenol in the subcritical water system.



Figure 6. Cont.



Figure 6. The kinetic behaviors of the selective conversion of phenol in subcritical water under different temperatures.

2.4. Developing a Kinetic Model for the Conversion of Phenol

In order to deepen the understanding of the conversion mechanism of phenol during the subcritical hydrothermal conversion process, it is necessary to develop a quantitative model for evaluating the effects of temperature and time on the phenol conversion. According to the literature [33] and the actual reaction process in this study, the possible conversion paths of phenol can be described as below.

Based on the data shown in Figure 6A–C, the side-reactions—including the generation reactions of benzene and cyclohexane—can be ignored. Thus, the selective conversion kinetic equations of phenol can be developed as below.

2.4.1. Model Development

The possible reaction paths of phenol during subcritical hydrothermal conversion was shown in Figure 7. Firstly, assume that there exist two main chemical reactions, i.e.,

$$Phenol + H_2 \xrightarrow{NiCo/\gamma - A_2O_3} Cyclohexanone,$$
(1)

$$Cyclohexanone + H_2 \xrightarrow{NiCo/\gamma - A_2O_3} Cyclohexanol.$$
(2)

As Equations (1) and (2) describe, firstly, phenol bonds with hydrogen to form cyclohexanone and then continuously converts to cyclohexanol. Considering the actual amounts of cyclohexanone and cyclohexanol at each moment, it can be easily deduced that the reaction rate of Equation (1) is much larger than the reaction rate of Equation (2). That is to say, Equations (1) and (2) can be rewritten as:

$$Phenol + H_2 \xrightarrow{NiCo/\gamma - A_2O_3} Cyclohexanol.$$
(3)

Due to the superfluous quantity of the H_2 in the reaction process, according to Equation (3), the selective conversion rates of phenol during subcritical hydrothermal conversion process can be described as below:

$$-\frac{dC_p}{dt} = k \cdot C_p^m,\tag{4}$$

where C_p represents the real-time concentration of phenol. *k* and *m* represent the reaction rate constant and order ($m \neq 1$), respectively.

Integrate Equation (4) to acquire:

$$C_p = \left[C_{p0}^{1-m} - (1-m) \cdot k \cdot (t-t_0)\right]^{\frac{1}{1-m}},$$
(5)

where C_{p0} and t_0 represent the initial concentration of phenol for cyclohexanol generation and the beginning time of the reaction, respectively.

Thus, the real-time concentration of cyclohexanol (i.e., C_l) can be calculated as:

$$C_l = C_{p0} - \left[C_{p0}^{1-m} - (1-m) \cdot k \cdot (t-t_0)\right]^{\frac{1}{1-m}}.$$
(6)

According to Arrhenius' equation, that is,

$$k = k_0 \cdot EXP\left(-\frac{Ea}{RT}\right),\tag{7}$$

where k_0 is the no-dimensional pre-exponential factor. *Ea* and *R* are the activity energy (J·mol⁻¹) and molar gas constant (~8.314 J·mol⁻¹·K⁻¹), respectively.

Insert Equation (7) into Equation (6), and obtain:

$$C_{l} = C_{p0} - \left[C_{p0}^{1-m} - (1-m) \cdot k' \cdot EXP\left(-\frac{Ea}{RT}\right)(t-t_{0})\right]^{\frac{1}{1-m}}.$$
(8)



Figure 7. The possible reaction paths of phenol during subcritical hydrothermal conversion.

2.4.2. Parameters Determination and Model Evaluation

For calculation of the parameters in Equation (8), the data of 19 samples of the phenol conversion process illustrated in Figure 6 were chosen. Using Equation (8) to fit them, the values of C_{p0} , k', m, Ea, and t_0 were obtained and are listed in Table 2.

Parameter	C_{p0} (mol/L)	k'	т	<i>t</i> ₀ (min)	<i>Ea</i> (kJ/mol)
Value	0.0864	317.13	1.15	0	37.82

Integrating the calculated parameters into Equation (8), the predicted value of C_l can be obtained. From Figure 8A, it is observed that there was a correlation between the predicted value and the measured value with the R-squared value of 0.9703, which verifies that the quantification model is robust. To study the prediction of the model's robustness, the relative deviation (RD) of the predicted and measured values at different temperature and time are described in Figure 8B. In Figure 8B, it can be found that most of the RD data of predicted values was within ~6.0%, which indicates that the temperature had little effect on the results. Thus, with the initial reaction conditions (e.g., water density, phenol addition, mass ratio of phenol and catalyst, etc.), the developed kinetic model should be suitable for the description of the selective conversion process of phenol. Moreover, it should be pointed out that with a change of initial reaction conditions as mentioned above, the parameters in the quantification model should be re-calculated for re-monitoring the conversion process.



Figure 8. (**A**) The correlation between the predicted and measured data; (**B**) Relative deviation (RD) of predicted values of cyclohexanol selectivity under different temperatures.

3. Experiments

3.1. Materials

 $Co(NO_3)_2 \cdot 6H_2O$, Ni(NO₃)₂ $\cdot 6H_2O$ and γ -Al₂O₃ were purchased from LXHG (Shandong, China). Phenol was purchased from Sigma-Aldrich. The experimental equipment used in this work was described in detail in our previous work [34].

3.2. Catalyst Preparation

The Ni–Co/ γ -Al₂O₃ catalysts were synthesized by the sequential impregnation method. In a typical synthesis, 1.0 g γ -Al₂O₃ powder, a certain amount of Co(NO₃)₂·6H₂O, and 5 mL ultrapure water were added into a 100-mL beaker. The mixture was then stirred at 70 °C in a water bath for 2 h followed by drying for about 12 h at 105 °C in an oven. Then, the sample was calcined at 300 °C for 2 h. A similar procedure was performed when impregnating Ni(NO₃)₂·6H₂O. Finally, the reduction of catalysts was carried out in a furnace tube in the presence of H₂. The temperature was kept at 400 °C for 4 h. After cooling to room temperature, the prepared catalysts were collected for further use. All catalysts were prepared using the same procedures mentioned above.

It should be pointed out that a catalyst is named as "15 wt%Ni–xCo/ γ -Al₂O₃" in this study, in which "15 wt%" represents the weight percentage of active metal (Ni + Co)/ γ -Al₂O₃ and x is the mass ratio of Ni/Co.

3.3. Catalyst Characterization

The specific surface area was measured by BET method using a surface area analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA). Before the analysis, all samples were degassed at 300 °C for 3 h. A Bruker D8 Advance diffractometer system was used to carry out XRD analysis for catalysts. The operation was performed at 40 kV voltage and 40 mA current with Cu Ka radiation (1.5406 Å) and a graphite monochromator (Holland PANalytical Corporation, Eindhoven, Holland). The catalysts were observed in the 2θ range of 20–80° at a scanning speed of 2°·min⁻¹. XPS data were obtained from a ULVAC PHI 5000 Versa Probe-II instrument (Ulvac-Phi Corporation, Kanagawa, Japan). TEM diagrams of the catalysts were given by an FEI Tecnai G2 TF30 S-Twin transmission electron microscope (FEI Corporation, Eindhoven, Holland).

3.4. Phenol Hydrogenation

In a typical reaction process, 6.6 mg phenol, 0.66 mL water, and 6.6 mg catalyst were loaded into a 4 mL stainless steel cylinder reactor (Swagelok Company, Shanghai, China). The reactor was purged with 0.2 MPa hydrogen (99.999%) (gauge) three times and filled with 2 MPa H₂. The reactor was then placed into a sand bath maintained at the desired reaction temperature. After the reaction, the reactor was taken out from the sand bath and then cooled to room temperature. The hydrogenous products were analyzed by a gas chromatograph (Agilent 7820A, California, USA) with a flame ionization detector (FID) using a 30 m \times 0.320 mm stainless steel column (packed with 60 \times 80 mesh Carboxen 100 (Supelco)). The product yield and selectivity and estimate are defined as follows:

$$Yield (\%) = \frac{the \ moles \ of \ product}{the \ moles \ of \ phenol} \times 100\%, \tag{9}$$

$$Total mole yield = \sum_{i=1}^{4} Yield, (10)$$

$$Selectivity (\%) = \frac{the \ moles \ of \ product}{the \ moles \ of \ phenol \ consumed} \times 100\%.$$
(11)

4. Conclusions

In this work, Ni–xCo/ γ -Al₂O₃ catalysts were first prepared and characterized. Then, a catalyst with optimal activity (i.e., 15 wt%Ni–3Co/ γ -Al₂O₃) was selected and used for selective conversion of phenol (i.e., a lignin monomer) into cyclohexanol in a subcritical water medium. The kinetic results showed that the conversion yield of phenol increased with the increase of reaction time and temperature, and the main product was cyclohexanol. After reaching reaction equilibrium, all of the moles yield and the selectivity of cyclohexanol reached ~80% at different temperature and time, which indicated that 15 wt%Ni–3Co/ γ -Al₂O₃ powders could be a promising catalyst for the conversion of phenol in a subcritical water medium. A robustness model for describing the conversion of phenol was also developed and verified.

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