

Hydrodeoxygenation of lignin-derived phenolic compounds catalyzed by NiCo bimetallic catalyst supported by N-doped biochar and Al_2O_3

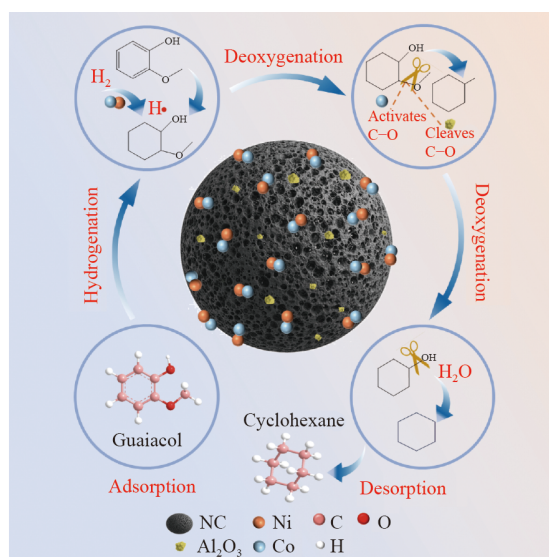
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Abstract: To achieve the efficient conversion of lignin-derived phenolic compounds into high-value hydrocarbon fuels, a series of NiCo bimetallic catalysts with N-doped biochar and Al_2O_3 composite supports ($\text{NiCo/NC-Al}_2\text{O}_3$) were designed and synthesized in this study. Comprehensive characterizations (XRD, TEM, XPS, H_2 -TPD) were conducted to reveal the superior catalytic activity in the HDO reaction of lignin-derived phenolic compounds. The optimized $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst exhibits good metal dispersion and excellent hydrogen dissociation adsorption capacity. Under mild reaction conditions (240°C , 1 MPa H_2), it achieves complete conversion of guaiacol and 99.9% selectivity of cyclohexane product, significantly outperforming the monometallic $\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$ and $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ catalysts. Comparative studies indicate a synergistic effect between Ni and Co, where the introduction of Co effectively promotes the hydrogenation of aromatic rings and the cleavage of C–O bonds. This study elucidates the regulatory mechanism of the Ni–Co synergistic effect on catalytic performance, providing new insights for the development of efficient non-noble metals HDO catalysts.

Key words: hydrodeoxygenation; NiCo bimetal; N-doped biochar; lignin; hydrocarbon fuels



With the global transition toward renewable and low-carbon energy systems, the efficient utilization of biomass resources has become a research hotspot in green chemistry and energy technologies^[1–2]. As the most abundant aromatic polymer with high carbon content in biomass, lignin is considered as an ideal precursor for the production of high-quality liquid fuels^[3–5]. However, the complex composition structure of lignin leads to its pyrolysis oils that are rich in phenols, aldehydes, ketones, and carboxylic acids, resulting

in high oxygen content, low heating value, and poor thermal stability^[6]. These drawbacks severely limit the direct application of bio-oil^[7–8].

Catalytic hydrodeoxygenation (HDO) is recognized as a key technology for upgrading bio-oil by removing oxygen-containing functional groups^[9]. HDO not only efficiently eliminates oxygenates from bio-oil, but also saturates C=C bonds and other unsaturated bonds, thereby greatly improving the energy density and stability of the upgrading

Received: 2025-10-29; Revised: 2025-11-26

Foundation items: Supported by the National Natural Science Foundation of China (52376217), Guangdong Natural Science Foundation (2024A1515011219) and Guangzhou Science and Technology Plan Project (2025D04J0008).

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DOI: 10.1016/S1872-5813(26)60649-4 CSTR: 32157.14.2097-213X.2026.JFCT.0004

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products^[10]. In the HDO catalytic systems, metal active sites are responsible for the adsorption and dissociation of hydrogen, providing active hydrogen species for subsequent hydrogenation reactions, while acid supports promote C–O bond cleavage and deoxygenation *via* their acid sites. As a result, HDO can efficiently convert phenols and other highly oxygenated components in bio-oil into low oxygen or even oxygen-free hydrocarbons, significantly enhancing their fuel quality^[11–13]. Guaiacol, as a representative model compound of lignin-derived pyrolysis oil, contains both aromatic rings and two types of C–O bonds, making it an ideal probe molecule for mechanistic studies and catalyst design for bio-oil HDO^[14].

Currently, noble metal catalysts (such as Ru, Pt and Pd) have been widely investigated for HDO due to their excellent HDO activities, enabling high selectivity of hydrocarbon products under mild conditions^[15–17]. For example, Khani et al.^[18] reported that the Ru/Al-MIL-53 metal-organic framework (MOF) catalyst achieved 100% conversion of guaiacol and 96.2% selectivity to cyclohexane at a catalyst-to-feed ratio of 1:1, 180 °C and 20 bar H₂. The catalysts presented outstanding stability, with little activity loss after five consecutive cycles. This demonstrates the great potential of noble metal catalysts for efficient HDO of phenolic compounds. However, the high cost and scarcity of noble metals limit their industrial application. In contrast, non-noble metals such as Ni, Co and Fe are promising alternatives for HDO due to their abundance and low cost^[19–20]. Nevertheless, non-noble metal catalysts usually require higher reaction temperatures and suffer from lower selectivity and more side reactions (e.g., C–C cleavage, alkyl transfer, and coking), which poses great challenge on their practical application in efficient HDO processes^[21].

Recently, Ni-Co bimetallic catalysts exhibited superior HDO performance compared to the monometallic counterparts, owing to their unique electronic and geometric synergistic effects^[22]. For instance, Zhang et al.^[23] loaded doped Ni-Co bimetallics onto Al₂O₃-TiO_x composite oxides for the HDO of guaiacol. Their study revealed that the Ti³⁺ species and oxygen vacancies introduced by the sol-gel method can synergistically interact with the Ni-Co alloy, significantly enhancing the adsorption and conversion of the reactant. Under mild conditions (200 °C, 1 MPa H₂), the optimized catalyst achieved complete conversion of guaiacol within 2 h, with cyclohexanol being the main product instead of cyclohexane, reaching a high selectivity of 93.7%. It is generally recognized that Ni⁰ sites facilitate hydrogen activation and aromatic ring hydrogenation, while the synergy between Ni and Co further lowers the energy barrier for this step^[24–25]. Zhang et al.^[23] attributed the high selectivity toward cyclohexanol to the relatively low reaction temperature and the lack of acid sites on the catalyst surface.

It is worth noting that besides the Ni-Co system, other non-noble bimetallic catalysts also have achieved significant progress recently. For example, Ye et al.^[26]

developed a Ni-Mo/HMB catalyst that leveraged the synergy between Ni-Mo nanoparticles and Lewis acid sites on the zeolite support, enabling complete conversion of methoxyphenol to cyclohexane under mild conditions at 140 °C. Zhao et al.^[27] reported a Ni₄Sn₁/MoO_x catalyst that achieved a conversion rate of furfural to 2-methylfuran as high as 99.8% at 170 °C by constructing Ni-Sn alloy and SnO_x Lewis acid sites. These published results demonstrate the great potential and research frontier in designing highly efficient HDO catalysts through precise modulation of bimetallic active centers and acid supports.

The acidity and surface structure of the support also play a crucial role in the deoxygenation process, as well as determining metal dispersion and affecting hydrogenation activity^[13]. N-doped carbon and Al₂O₃ are popular supports, which not only provides moderate acid sites to promote deoxygenation, but also enhances metal dispersion and anti-sintering ability through N anchoring^[28–29]. For example, Wu et al.^[30] developed a composite catalyst by anchoring Ni-Mo alloy on graphitic carbon nitride (g-C₃N₄) coated γ-Al₂O₃ (10Ni-5Mo/CN@γ-Al₂O₃), which achieved a high degree of deoxygenation (96.5%) and excellent selectivity to cycloalkanes during the lignin oil HDO at 240 °C and 3 MPa H₂. The mechanism analysis revealed that electron transfer within the Ni-Mo alloy and the strong interaction between g-C₃N₄ and the surface-anchored alloy facilitated H₂ dissociation and aromatic ring hydrogenation, while the formation of oxygen vacancies enhanced the adsorption and activation of oxygen-containing substrates, thus promoting deoxygenation reactions. Although this study provides a new strategy for constructing efficient non-noble metal catalysts for the HDO of bio oil into aviation fuels, the preparation of g-C₃N₄ needs a high cost, raising a big obstacle to the practical application. Therefore, the development of carrier materials that combine high performance with low cost is crucial for advancing the practical application of HDO technology. In recent years, biochar with high specific surface area and tunable pore structure has garnered significant attention in the field of catalysis due to its abundant sources, cost-effectiveness, and sustainability^[31–33], making it an ideal catalyst support^[34–35].

Based on the above background, this work designed and synthesized a N-doped biochar (NC) as one of the support components, by using biomass as the carbon source, which reduces the preparation cost significantly. Afterwards, the supported NiCo bimetallic catalysts of NiCo/NC-Al₂O₃ were prepared by co-precipitation method through introduction of Ni, Co and Al₂O₃ in one pot. The effect of Ni/Co molar ratio in the catalysts was systematically investigated, and the HDO reaction conditions were also optimized. By comparing the catalytic performance and product distribution under different catalyst compositions and reaction conditions, the synergistic effect of Ni-Co and its regulation of the reaction pathways are elucidated, providing theoretical guidance and experimental basis for the rational design of efficient non-noble metal HDO catalysts.

1 Materials and methods

1.1 Materials

All chemicals used in this study, including ZnCl_2 , K_2CO_3 , urea, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaOH , HCl and *n*-octane, were purchased from Aladdin Reagent Co., Ltd. The rice husk was obtained from a wholesale market in Guangzhou, Guangdong Province.

1.2 Catalyst preparation

Preparation of hydrochar: A mixture of 8 g rice husks and 3.4 g zinc chloride was added to 100 mL deionized water (Zn content: 20%) and stirred for 2 h, followed by ultrasonication for 30 min to achieve homogeneous dispersion. The suspension was transferred into a 200 mL Teflon-lined autoclave, sealed in a stainless-steel reactor, and maintained at 220 °C for 15 h. After natural cooling to room temperature, the resulting solid was washed repeatedly with deionized water until neutral pH was achieved. The product was then dried at 85 °C in an air-blowing drying oven for 12 h to obtain the hydrochar.

Preparation of N-doped carbon: The hydrochar, potassium carbonate, and urea were weighed in a mass ratio of 1:1:1 and placed in a beaker. Then, 30 mL deionized water was added, and the beaker was sealed with plastic film and stirred at a constant speed of 300 r/min for 6 h to ensure thorough impregnation of the activators. After impregnation, the mixture was dried at 105 °C for 12 h. The dried sample was then placed in a tube furnace and purged with nitrogen for 15 min to establish an inert atmosphere. Subsequently, the temperature was raised to 800 °C at a heating rate of 5 °C/min under a nitrogen flow of 60 mL/min and held for 1 h for activation. The activated product was rinsed with 1 mol/L HCl to remove inorganic salts, followed by repeated washing with deionized water until neutrality. Finally, the sample was dried at 85 °C to obtain NC.

Preparation of $\text{NiCo/NC-Al}_2\text{O}_3$ Catalysts: Taking the synthesis of $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ with a total metal loading of 10% as an example: 0.5 g of NC was dispersed in 30 mL deionized water in a single-neck round-bottom flask. Separately, 0.099 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.838 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.396 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 12 mL deionized water, and the solution was drawn into a 15 mL syringe. Then, 0.75 g of NaOH was dissolved in 12 mL deionized water and loaded into another syringe. The flask was placed in an oil bath at 85 °C under stirring. The metal salt solution and NaOH solution were simultaneously injected into the flask using a syringe pump at a rate of 1 mL/min over 12 min. After injection, stirring was continued for 10 min, and the pH was adjusted to 10 using pH test paper. The mixture was reacted for 12 h, then filtered, and the solid was dried at 85 °C. The dried sample was reduced under a H_2 flow (80 mL/min) at 600 °C for 1 h with a heating rate of 5 °C/min, yielding the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst. For comparison, monometallic catalysts

$\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$ and $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ were also prepared using the same procedure with a total metal loading of 10%. Specifically, no Co salt was added for $\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$, and no Ni salt was used for $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$. All other steps remained unchanged. The similar preparation procedures were also used to prepare $\text{Ni}_5\text{Co}_5/\text{NC-Al}_2\text{O}_3$, $\text{Ni}_6\text{Co}_4/\text{NC-Al}_2\text{O}_3$, $\text{Ni}_7\text{Co}_3/\text{NC-Al}_2\text{O}_3$ and $\text{Ni}_9\text{Co}_1/\text{NC-Al}_2\text{O}_3$ catalysts, with the total metal loading of 10% and the NC to Al_2O_3 weight ratio of 1:1. In addition, to investigate the effect of Al_2O_3 and NC loading amounts on the catalyst performance, the three catalysts of $\text{Ni}_8\text{Co}_2/\text{C-Al}_2\text{O}_3$ (N-free), $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ (1:2) and $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ (2:1) were prepared by using the same method.

1.3 Catalyst characterization

In this study, the nitrogen adsorption-desorption isotherms at 77 K were recorded using a Micromeritics ASAP 2460 analyzer. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method, the average pore diameter was extracted from the desorption branch using the Barrett-Joyner-Halenda (BJH) method, and the total pore volume was obtained through a single-point adsorption procedure. X-ray powder diffraction (XRD) analysis was carried out using a Shimadzu XRD-6000 instrument in the 2θ range of 5°–90° with $\text{Cu K}\alpha$ radiation (operating at 40 kV and 30 mA, with a wavelength of 0.15406 nm). The crystallite size of the catalyst was calculated according to the Debye-Scherrer equation:

$$D = \frac{K \times \lambda}{\beta \times \cos \theta} \quad (1)$$

where D is the average crystallite size (Å), K is the Scherrer constant (0.89), λ is the X-ray wavelength (1.5406 Å), θ is the Bragg angle, and β is the full width at half maximum of the diffraction peak. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) analysis were performed using a Thermo Fisher Quattro S device. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was conducted on the instrument of OPTIMA 8000. Additionally, transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and scanning TEM (STEM) images were obtained using a Thermo Talos F200S instrument. The temperature-programmed desorption of H_2 (H_2 -TPD) was carried out in a U-shaped quartz reactor on a ChemStar instrument to study the hydrogen activation and adsorption properties of the catalyst. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific ESCALAB 250Xi system equipped with an $\text{Al K}\alpha$ excitation source (1486.6 eV), with the C 1s peak at 284.8 eV used as the reference for charge correction.

1.4 HDO of phenolic compounds and original lignin pyrolysis oil

HDO reaction of phenolic compounds was carried out in

a 50 mL high-pressure reactor made of 316 L stainless steel. The specific experimental procedure is as following. First, 0.1 g of the phenolic compound was dissolved in 20 mL of *n*-octane, and then 0.05 g of the catalyst was added. After sealing the reactor, the residual air was purged by three cycles of hydrogen charging and discharging, with the pressure maintained at 1 MPa each time. Subsequently, under programmed control, the system was heated to the preset temperature at a rate of 3 °C/min while being stirred at 400 r/min, and this condition was maintained for 4 h.

For the upgrading treatment of lignin-derived bio-oil, 3.0 g of crude lignin bio-oil was mixed with 20 mL of *n*-octane to extract the phenolic compounds. Then, the HDO reaction of the lignin pyrolysis oil was conducted following the same steps as above. After the reaction, the reactor was allowed to cool naturally to room temperature. The liquid products were collected by filtration and analyzed for their chemical composition using a gas chromatography-mass spectrometry (GC-MS, Thermo Fisher Scientific Trace 1300) equipped with a TG-5 Sil MS capillary column (30 m×0.25 mm×0.25 µm film thickness). The product selectivity was calculated based on the ratio of peak areas, and the substrate conversion and selectivity were determined using the following formulas:

$$\text{Conversion (\%)} = \frac{\text{Moles}_{\text{initial GUA}} - \text{Moles}_{\text{remaining GUA}}}{\text{Moles}_{\text{initial GUA}}} \times 100\% \quad (2)$$

$$\text{Selectivity (\%)} = \frac{\text{Moles}_{\text{product}_i}}{\sum \text{Moles}_{\text{product}}} \times 100\% \quad (3)$$

2 Results and discussion

2.1 Catalyst characterization

The crystal structure of the catalyst was characterized by XRD. The results are shown in Figure 1 and all catalysts present wide diffraction peaks, indicating their amorphous characteristics. The monometallic Ni₁₀/NC-Al₂O₃ catalyst exhibits three distinct diffraction peaks at $2\theta = 44.5^\circ$, 51.8° and 76.4° , corresponding to the (111), (200) and (220) planes of Ni (PDF#04-0850), respectively. The monometallic Co₁₀/NC-Al₂O₃ catalyst shows (111), (200) and (220) characteristic peaks of Co (PDF#15-0806) at $2\theta = 44.2^\circ$, 51.5° and 75.8° . For the Ni₈Co₂/NC-Al₂O₃ catalyst, its diffraction peaks appear at 44.3° , 51.6° and 76.3° . These peaks are between the standard peaks of pure Ni and pure Co, and no diffraction peaks of independent Ni or Co species are observed. The main peak (44.3°) of NiCo (111) phase is offset by 0.2° from the low angle compared with pure Ni (44.5°). And it is also slightly changed from the pure Co (44.2°), due to the offset of the diffraction peak of its (111) grain plane to the low peak, which indicates the formation of Ni-Co alloy^[36]. In addition, according to the Debye-Scherrer formula for the (111) crystal plane, the average grain size of the alloy nanoparticles in Ni₈Co₂/NC-

Al₂O₃ is about 9.36 nm, which is smaller than that of the single metals Ni₁₀/NC-Al₂O₃ (10.42 nm) and Co₁₀/NC-Al₂O₃ (12.68 nm), indicating that the introduction of bimetals can effectively inhibit the sintering of metal particles and promote the formation of smaller and more dispersed alloy nanoparticles.

The distribution and morphology of Ni and Co metal particles in the NiCo/NC-Al₂O₃ catalysts were further investigated by TEM. The particles of Ni₈Co₂/NC-Al₂O₃, Ni₁₀/NC-Al₂O₃ and Co₁₀/NC-Al₂O₃ catalysts are subjected to statistical analysis, yielding average particle sizes of 9.59, 10.51 and 12.46 nm, respectively. Among them, the Ni₈Co₂/NC-Al₂O₃ catalyst not only possesses the smallest average particle size but also exhibits good dispersion without significant agglomeration. This trend of particle size reduction is consistent with the XRD results. High-resolution TEM (HR-TEM) images (Figure 2(a)) reveal clear lattice fringes within individual nanoparticles of the Ni₈Co₂/NC-Al₂O₃ catalyst. The lattice spacing of the Ni₈Co₂/NC-Al₂O₃ (0.210 nm) is larger than that of Ni₁₀/NC-Al₂O₃ (0.208 nm) and Co₁₀/NC-Al₂O₃ (0.206 nm). This lattice expansion phenomenon is likely due to the formation of a Ni-Co alloy solid solution. Given the slight difference in atomic radii between Ni and Co, the incorporation of the larger Co atoms into the Ni lattice to form a substitutional solid solution expands the lattice, leading to an increase of the interplanar spacing^[37]. Furthermore, EDS mapping (Figure 2(i)) further confirms the dispersion state of the metal particles in the Ni₈Co₂/NC-Al₂O₃ catalyst. It is observed that the active metals, Ni (purple) and Co (blue), are densely dispersed on the support surface as small and uniform particles. The comparison of the spatial distributions of Ni and Co signals shows a high degree of overlap, which also verifies the formation of a Ni-Co alloy^[38]. Meanwhile, the morphology of the catalyst is also examined by SEM. As shown in Figure 2(g), (h), the Ni₈Co₂/NC-Al₂O₃ catalyst clearly exhibits a porous flocculent structure with a rough surface. Such a loose and porous morphology not only implies a relatively large specific surface area but also provides abundant attachment sites for the anchoring and dispersion of metal nanoparticles.

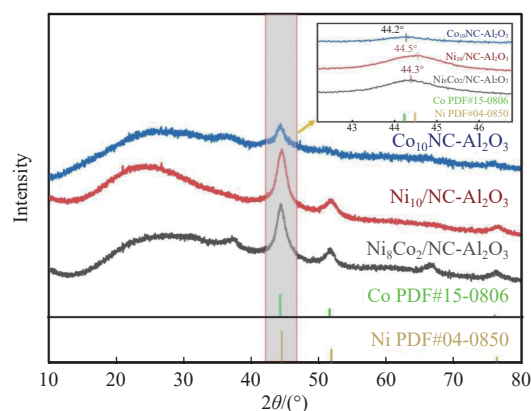


Fig. 1 XRD patterns of the different NiCo/NC-Al₂O₃ catalysts

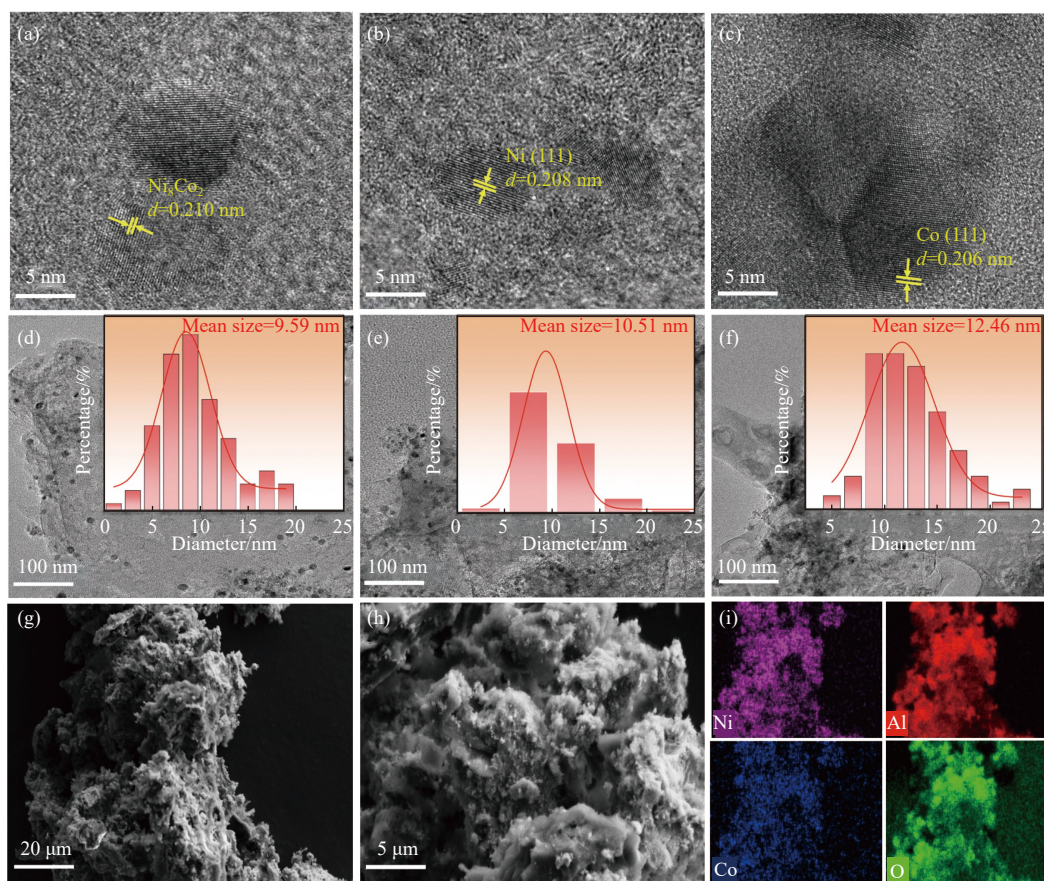


Fig. 2 TEM images and corresponding particle size distributions of $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ ((a), (d)), $\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$ ((b), (e)) and $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ ((c), (f)); SEM images ((g), (h)) and EDS energy spectrum (i) of $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$

The structural properties of the $\text{NiCo}/\text{NC-Al}_2\text{O}_3$ catalysts were characterized by N_2 physisorption-desorption experiments. As shown in Table 1, all catalysts exhibit relatively high specific surface areas and well-developed pore structures. Their specific surface areas follow the order of $\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$ ($1062.88 \text{ m}^2/\text{g}$) > $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ ($813.15 \text{ m}^2/\text{g}$) > $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ ($558.30 \text{ m}^2/\text{g}$). Notably, this bimetallic catalyst possesses the largest pore volume (1.08 mL/g) and a slightly larger average pore size (8.23 nm). The differences in specific surface area, pore volume and pore size among these catalysts are mainly attributed to the loading of the active metals Ni and Co, as well as the metal-support interactions. After the introduction of Ni and Co, their corresponding oxide and metal nanoparticles tend to occupy part of the original pores of the support, leading to a reduction in specific surface area. The highest specific surface area of $\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$ catalyst suggests that Ni species interact strongly with the support, which inhibits their migration and aggregation during H_2 reduction, resulting in a highly dispersed state on the support^[39]. In

contrast, the tendency of Co species to aggregate into larger particles on the support in the $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ catalyst, significantly reduces its the specific surface area^[40–41]. The large pore size and pore volume of the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst will provide advantage to the HDO reaction. Moreover, the actual metal contents of Ni and Co in the catalysts were determined by ICP-AES. As summarized in Table 1, Ni content in $\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$ is 8.67%, while the Co content in $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ is 9.22%. For the bimetallic $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst, the contents of Ni and Co are 7.91% and 1.96%, respectively, which are close to their theoretical values.

The elemental composition and valence states of the $\text{NiCo}/\text{NC-Al}_2\text{O}_3$ catalyst were characterized by XPS. As shown in Figure 3(a), four distinct peaks are observed in the Ni $2p_{3/2}$ XPS spectrum of the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst, with binding energies located at 853.7, 857.0, 860.8 and 863.5 eV, corresponding to metallic Ni^0 , Ni^{3+} , Ni^{2+} and a satellite peak of Ni^{2+} , respectively^[42].

Table 1 Structural and surface properties of the different catalysts

Catalyst	Specific surface area ^a /($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ^b /($\text{mL} \cdot \text{g}^{-1}$)	Pore diameter ^b /nm	Ni content ^c w/%	Co content ^c w/%
$\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$	1062.88	0.86	7.87	8.67	—
$\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$	813.15	1.08	8.23	7.91	1.96
$\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$	558.30	0.77	7.95	—	9.22

^a: Data measured by BET method; ^b: Data measured by BJH method; ^c: Data measured by ICP-AES.

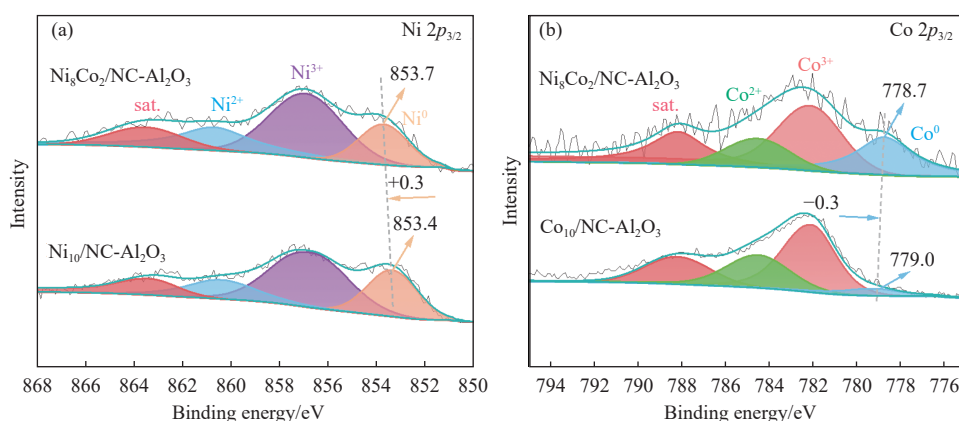


Fig. 3 XPS profiles in the Ni $2p_{3/2}$ (a) and Co $2p_{3/2}$ (b) regions of different catalysts

Compared with the monometallic $\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$ catalyst (Ni^0 : 853.4 eV), the binding energy of Ni^0 is shifted positively by 0.3 eV. The Ni sites, having a low extranuclear electron density, likely exhibit an upshifted d -band center, which enhances their ability to adsorb and activate oxygen atoms and π -electrons in the substrate (such as C=O and the aromatic ring). This is particularly beneficial for cleaving the critical C–O bond^[43]. As shown in Figure 3(b), the fitting of the Co $2p_{3/2}$ XPS spectrum reveal four peaks in the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst, located at 778.7, 782.1, 784.6 and 788.1 eV. These peaks are assigned to Co^0 , Co^{3+} , Co^{2+} and a satellite peak of Co^{2+} , respectively^[44]. Compared with the monometallic $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ catalyst (Co^0 : 779.0 eV), a negative shift of 0.3 eV towards lower binding energy is presented. This shift indicates electron transfer from Ni to Co on the surface, leading to an increased electron cloud density around Co. The electron-enriched Co facilitates the efficient activation of H_2 , generating a large amount of active hydrogen species to improve the HDO reaction^[38].

The hydrogen activation capacity of the catalysts was evaluated using H_2 -TPD. As shown in Figure 4, the H_2 -TPD peak temperatures of the three catalysts exhibit distinct differences. The $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ catalyst shows the highest peak temperature at 589.5 °C, indicating the strongest hydrogen adsorption on monometallic Co sites.

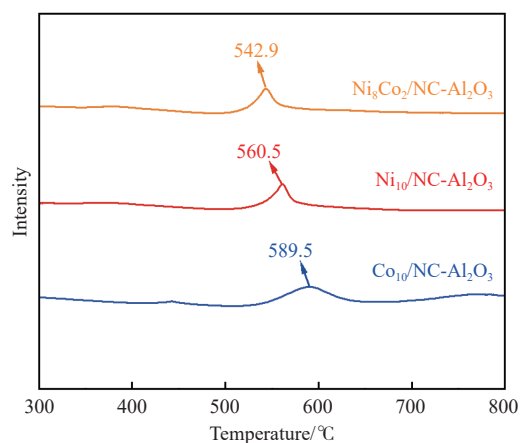


Fig. 4 H_2 -TPD profiles of different NiCo/NC- Al_2O_3 catalysts

The $\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$ catalyst exhibits a lower peak temperature of 560.5 °C, suggesting a weaker hydrogen adsorption strength compared to the Co-based catalyst. In contrast, the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ bimetallic catalyst demonstrates the lowest peak temperature at only 542.9 °C, implying the weakest hydrogen adsorption interaction with the catalyst surface. This phenomenon may be attributed to electron transfer between Ni and Co metals during alloy formation due to the differences of their electronegativity, which alters the electronic structure of the catalytic metal centers and weakens their hydrogen adsorption strength. As a result, hydrogen desorption occurs at a lower temperature^[45]. Among the catalysts, although $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ possesses the highest hydrogen adsorption capacity, its excessively high desorption temperature leads to low reactivity of the hydrogen species. In comparison, the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst, through synergistic effect and alloy formation, effectively reduces the hydrogen adsorption strength while retaining high adsorption capacity. This optimized hydrogen adsorption characteristic enables the catalyst surface to achieve a high concentration of active hydrogen species, thereby accelerating the rate of HDO reaction.

2.2 Catalytic HDO of guaiacol

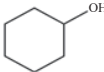
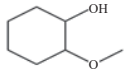
The product distribution from the HDO reaction of guaiacol over NiCo/NC- Al_2O_3 catalysts with different Ni/Co molar ratios at 240 °C and 1.0 MPa H_2 for 4 h is presented in Table 2. The conversion of guaiacol reaches 99.9% for all the catalysts, which indicates that all the catalysts possess high catalytic activity. However, significant differences in product selectivity are observed among the different catalysts. For the monometallic catalysts, $\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$ and $\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$ produce 50.5% and 31.9% cyclohexanol, respectively. This suggests that they primarily promote the hydrogenation of aromatic rings, but the subsequent deoxygenation capability is severely insufficient, causing the reaction to halt at the hydrogenated intermediate stage. Notably, the monometallic Co catalyst ($\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$) exhibits higher cyclohexane selectivity than the monometallic Ni catalyst ($\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$),

indicating that Co metal has greater potential than Ni in promoting the deoxygenation reaction. However, its single active site is still insufficient to efficiently complete the full conversion pathway from guaiacol to cyclohexane. When a small amount of Co is introduced to form $\text{Ni}_9\text{Co}_1/\text{NC-Al}_2\text{O}_3$, its product distribution (cyclohexane 49.7%, cyclohexanol 50.3%) is very close to that of the monometallic Ni catalyst (cyclohexane 49.5%, cyclohexanol 50.5%). This shows that the introduction of a trace amount of Co did not significantly alter the essential nature of the catalytic sites. With a continued increase in Co content, the performance peaks at Ni/Co ratio of 8:2 ($\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$), achieving 99.9% selectivity towards cyclohexane. This indicates that at this specific ratio, Ni and Co likely form the most suitable alloy structure. Ni, with its excellent hydrogenation capability, is responsible for the rapid hydrogenation of the aromatic ring and intermediates, while Co exhibits stronger ability to activate and cleave C–O bonds^[46]. The Ni–Co bimetallic system, through synergistic effects, establishes an efficient and continuous reaction pathway from guaiacol *via* intermediates to cyclohexane, preventing the accumulation of cyclohexanol. However, when the Co content is further increased to form $\text{Ni}_6\text{Co}_4/\text{NC-Al}_2\text{O}_3$ and $\text{Ni}_5\text{Co}_5/\text{NC-Al}_2\text{O}_3$, the cyclohexane selectivity decreases to 74.5% and 27.0%, respectively. This is possibly because introducing excessive Co alters the electronic properties of the alloy, making its behavior more akin to the monometallic Co catalyst (favoring cyclohexanol formation), thereby weakening the synergistic effect between Ni and Co. The $\text{Ni}_5\text{Co}_5/\text{NC-Al}_2\text{O}_3$ catalyst even shows lower cyclohexane selectivity than the monometallic Co catalyst, indicating that an inappropriate Ni/Co ratio can lead to detrimental interactions, inhibiting the deoxygenation step. Therefore, it is evident that there is an optimal ratio between Ni and Co when forming an alloy. At the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ ratio, the synergistic effect between the two metals is maximized. $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$

catalyst possesses not only excellent hydrogenation capability but also superior deoxygenation activity, enabling the efficient conversion of guaiacol to the target product of cyclohexane. Moreover, the loading amounts of Al_2O_3 and NC also have a significant impact on the catalyst performance. As shown in Table 2, under the optimal Ni/Co molar ratio (8:2), ratio variations of NC to Al_2O_3 in the support noticeably alter the product distribution. When the Al_2O_3 proportion is increased, the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ (1:2) presents a cyclohexane selectivity of 89.9%. Whereas when the Al_2O_3 proportion is decreased, the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ (2:1) presents a decreased cyclohexane selectivity of 42.5%, with the cyclohexanol selectivity increasing to 55.6%. This result indicates that a sufficient Al_2O_3 content in the support is crucial for providing the necessary acidity to effectively promote C–O bond cleavage. Furthermore, comparing the N-free $\text{Ni}_8\text{Co}_2/\text{C-Al}_2\text{O}_3$ (cyclohexane selectivity 86.3%) with the N-doped $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ (cyclohexane selectivity 99.9%), it can be concluded that N-doping optimizes the electronic structure of the metal centers, synergistically enhancing the deoxygenation efficiency of the catalyst.

The effect of reaction time on the HDO reaction over the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst was also investigated. As shown in Figure 5(a), after 1 h of reaction, the conversion of guaiacol reaches 96.1%, with cyclohexane (42.5%) and cyclohexanol (46.4%) as the main products, along with a small amount of the intermediate methoxy cyclohexanol (11.1%). This indicates that in the initial stage of the reaction, the hydrogenation of the substrate's aromatic ring and direct deoxygenation proceed simultaneously. When the reaction time is extended to 2 h, the conversion increases to 99.3%, and cyclohexane becomes the dominant product (87.5%), while cyclohexanol decreases to 12.5%. Methoxy cyclohexanol is completely consumed and converted into a small amount of cyclohexanol.

Table 2 HDO performance of guaiacol over different NiCo/NC- Al_2O_3 catalysts

Catalyst	Conversion/%	Product selectivity/%		
				
$\text{Ni}_5\text{Co}_5/\text{NC-Al}_2\text{O}_3$	99.9	27.0	73.0	–
$\text{Ni}_6\text{Co}_4/\text{NC-Al}_2\text{O}_3$	99.9	74.5	25.5	–
$\text{Ni}_7\text{Co}_3/\text{NC-Al}_2\text{O}_3$	99.9	81.9	18.1	–
$\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$	99.9	99.9	–	–
$\text{Ni}_9\text{Co}_1/\text{NC-Al}_2\text{O}_3$	99.9	49.7	50.3	–
$\text{Ni}_{10}/\text{NC-Al}_2\text{O}_3$	99.9	49.5	50.5	–
$\text{Co}_{10}/\text{NC-Al}_2\text{O}_3$	99.9	68.1	31.9	–
$\text{Ni}_8\text{Co}_2/\text{C-Al}_2\text{O}_3$	99.9	86.3	13.7	–
$\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ (1:2)	99.9	89.9	10.1	–
$\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ (2:1)	99.9	42.5	55.6	1.9

Condition: 20 mL *n*-octane, 0.1 g guaiacol, 0.05 g catalyst, 240 °C, 1 MPa H_2 , 4 h. $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst has the weight ratio of NC to Al_2O_3 of 1:1. $\text{Ni}_8\text{Co}_2/\text{C-Al}_2\text{O}_3$ catalyst is used the N-free carbon support. $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ (1:2) catalyst means that the weight ratio of NC to Al_2O_3 is 1:2.

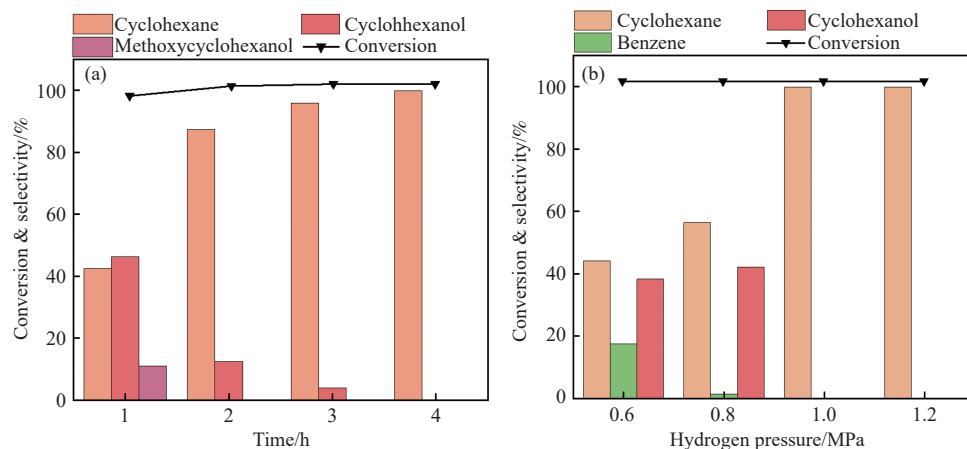


Fig. 5 Effects of (a) reaction time, (b) reaction pressure on the HDO of guaiacol

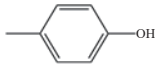
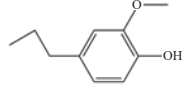
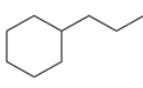
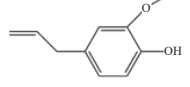
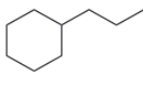
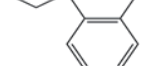
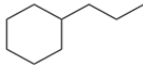
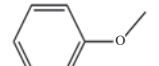
After 4 h, the reaction is complete finished, and the product is almost exclusively cyclohexane (99.9%). This evolution of products indicates that both methoxy cyclohexanol and cyclohexanol are intermediates in the reaction pathway. The overall reaction follows a consecutive hydrogenation route of guaiacol, methoxy cyclohexanol, cyclohexanol to cyclohexane^[47]. Furthermore, hydrogen pressure has a significant influence on the selectivity of the final product. As shown in Figure 5(b), under a fixed reaction time of 4 h, when the H₂ pressure is increased from 0.6 to 1.0 MPa, the selectivity towards cyclohexane markedly improves from 44.2% to 99.9%. Concurrently, the partially hydrogenated product (cyclohexanol) decreases, and the over-dehydroaromatization product (benzene) disappears completely. When the H₂ pressure is further increased to 1.2 MPa, the reaction process is almost unaffected, with no significant changes in conversion or product selectivity. This demonstrates that a H₂ pressure of 1.0 MPa enables the complete conversion of guaiacol to cyclohexane, which is at

a relatively low hydrogen pressure compared to other reported works^[48–49].

2.3 HDO of other phenolic compounds

To investigate the universality of the Ni₈Co₂/NC-Al₂O₃ catalyst, the HDO of various phenolic compounds was tested as well, including eugenol, *p*-cresol, 2-propylphenol, 2-methoxy-4-propylphenol, and anisole. The reaction results are summarized in Table 3. Under the conditions of 1 MPa H₂ and 240 °C for 4 h, all the substrates achieve complete conversion. The catalyst effectively overcomes the steric hindrance imposed by alkyl chains or methoxy groups, enabling complete hydrogenation of the aromatic ring and thorough removal of all oxygen-containing functional groups. The corresponding alkane products of propylcyclohexane and cyclohexane are obtained with selectivity as high as 99.9%.

Table 3 HDO results of other typical phenolic compounds on Ni₈Co₂/NC-Al₂O₃ catalysts

Substrate	Conversion/%	Product selectivity/%
	99.9	 99.9
	99.9	 99.9
	99.9	 99.9
	99.9	 99.9
	99.9	 99.9

Condition: 20 mL *n*-octane, 0.1 g reaction substrate, 0.05 g catalyst, 1 MPa H₂, 4 h, 240 °C.

Overall, the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst exhibits excellent HDO activity toward various phenolic compounds at 240°C under 1 MPa H_2 , effectively cleaving the $\text{C}(\text{Ar})\text{-OH}$ bonds and hydrogenating the aromatic rings. Even when applied to complex phenolic molecules bearing alkyl chains, the catalyst still maintains extremely high selectivity toward complete hydrodeoxygenation.

To evaluate the stability of the $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst, a four-cycle recycling test was conducted. The results are shown in Figure 6(a). The catalyst maintains a consistent guaiacol conversion rate of $>99.9\%$ throughout all four cycles, indicating that the primary active sites responsible for the HDO reaction retain excellent activity. However, the selectivity for the target product of cyclohexane shows a noticeable decline in the subsequent cycles. It decreases from 99.9% selectivity initially to 97.8% in the third cycle and 93.8% in the fourth cycle. To investigate the cause of the decrease in cyclohexane selectivity during the recycling test, we performed SEM and XRD characterization of the fresh and spent $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalysts. SEM images

(Figure 6(b)) show that the fresh catalyst has a uniform particle distribution and a loose structure, while the spent sample exhibits some degree of particle aggregation, with blurred boundaries and a slight increase of particle size, indicating slight sintering of the metal nanoparticles during the reaction. XRD patterns (Figure 6(c)) further clarify the structural changes. Compared to the fresh catalyst, the characteristic diffraction peak positions of the spent sample don't show significant shifts, but a narrowing of the full width at half maximum is observed. Referring to the Ni (PDF#04-0850) and Co (PDF#15-0806) standard cards, this narrowing phenomenon is mainly attributed to slight grain growth, with no significant changes in the alloy structure detected. This result suggests that due to slight sintering, the geometric structure of the Ni-Co alloy has undergone moderate adjustments, which may have affected the electronic structure and reduced the efficiency of Co sites in C–O bond cleavage, ultimately leading to a gradual decrease in cyclohexane selectivity.

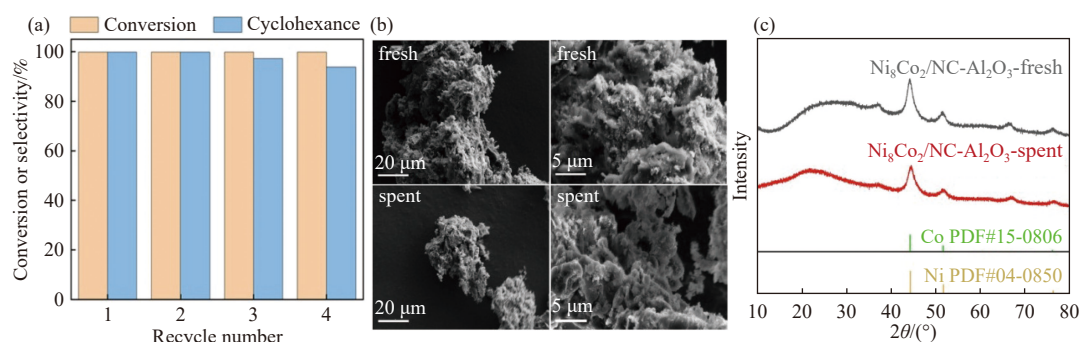


Fig. 6 (a) Catalytic performance of $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ over four cycles, (b) SEM images of the fresh catalyst and the spent catalyst after four cycles, (c) XRD patterns of the fresh and spent catalysts after four cycles

3 Conclusions

This study prepared a NiCo bimetallic catalyst supported on N-doped biochar and alumina ($\text{NiCo}/\text{NC-Al}_2\text{O}_3$) using the co-precipitation method and systematically investigated its catalytic performance in the HDO of lignin-derived phenolic compounds. Comprehensive characterization results reveal that a stable alloy phase is formed between Ni and Co, and the electron transfer from Ni to Co effectively optimizes the hydrogen adsorption properties of the catalyst. Among the HDO tests, $\text{Ni}_8\text{Co}_2/\text{NC-Al}_2\text{O}_3$ catalyst exhibits the best catalytic performance, achieving complete conversion of guaiacol with a cyclohexane selectivity of up to 99.9% under mild reaction conditions of 240°C and 1 MPa H_2 for 4 h, significantly surpassing the performance of monometallic catalysts. In the recycle stability tests, the catalyst maintains high catalytic activity after four reuse cycles, demonstrating outstanding structural stability. This study shows that constructing a NiCo bimetallic alloy structure can effectively modulate the electronic properties of active sites, leading to a synergistic enhancement of hydrogenation and deoxygenation activities. This work

provides new design insights and experimental evidence for the development of efficient and stable non-noble metals HDO catalysts.

Declaration of Competing Interest

The authors declare no conflict of interest.

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氮掺杂生物炭与 Al_2O_3 复合载体负载 NiCo 双金属催化木质素衍生酚类加氢脱氧研究

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摘 要: 为实现木质素衍生酚类化合物向高价值烃类燃料的高效转化, 本研究设计并合成了一系列以氮掺杂生物炭与 Al_2O_3 为复合载体的 NiCo 双金属催化剂 ($\text{NiCo}/\text{NC}-\text{Al}_2\text{O}_3$)。通过 XRD、TEM、XPS、 H_2 -TPD 表征揭示了其在木质素酚类加氢脱氧(HDO)反应中的优越催化活性。优化后的 $\text{Ni}_8\text{Co}_2/\text{NC}-\text{Al}_2\text{O}_3$ 催化剂具有良好的金属分散性和优异的氢解离吸附能力。在 240 °C、1 MPa H_2 条件下, 该催化剂可实现愈创木酚的完全转化, 并对环己烷产物具有 99.9% 的选择性, 其性能显著优于单金属 $\text{Ni}_{10}/\text{NC}-\text{Al}_2\text{O}_3$ 和 $\text{Co}_{10}/\text{NC}-\text{Al}_2\text{O}_3$ 催化剂。对比研究表明, Ni 与 Co 之间存在协同效应, Co 的引入有效促进了芳环加氢与 C–O 键断裂。本研究阐明了 Ni-Co 协同效应对催化性能的调控机理, 为开发高效非贵金属 HDO 催化剂提供了新思路。

关键词: 加氢脱氧; NiCo 双金属; 氮掺杂生物炭; 木质素; 烃类燃料

中图分类号: TQ517; O643.36

文献标识码: A

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