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Efficient Lignin Depolymerization Process for Phenolic Products with Lignin-Based Catalysts and Mixed Solvents

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ABSTRACT: Due to their diverse functional groups and structural composition, carbon-based catalysts exhibit superior performance in various catalytic reaction systems, such as hydrogenolysis, hydrogenation, and oxidation. Herein, we propose an effective strategy of lignin liquid-phase depolymerization by applying the designed lignin-based carbon catalysts to produce aromatic chemicals. A series of Ni–Mo bimetallic carbon-based catalysts were synthesized to explore the effect of different preparation methods on the catalytic activity. The results demonstrate that the embedded Ni–Mo/C-_{WMO} catalyst with multi-active sites of Ni, MoO₃, and Mo₂C results in a prominent catalytic effect on lignin depolymerization. The Ni–Mo/C-_{WMO} catalyst can achieve a lignin



conversion of 87.62% with a 42.25% monophenol yield in the methanol and water system. With the synergistic contribution of multiple active sites of the catalyst and the mixed-solvent system (water, methanol, and 1, 4-dioxane), a remarkably high yield of 62.95% of mono-phenolic compound was achieved at 260 °C and 3 MPa N₂ with a reaction time of 4 h. The selectivity of 2-methoxy-4-methylphenol and 2-methoxy-4-ethylphenol in liquid products was 40.85 and 36.42%, respectively. Vanillin, a typical product from lignin depolymerization reported in the literature, was further degraded to monophenol in this system. The outcomes also confirmed that the in situ hydrogen production system of methanol and water coupled with 1,4-dioxane facilitated the lignin depolymerization significantly.

1. INTRODUCTION

In recent years, renewable energy has become a promising candidate to replace fossil energy. Among them, bio-organic carbon inherent in biomass is considered as an abundant and cheap source equivalent to fossil fuels.¹ Lignin, one of the major components of lignocellulosic biomass and the largest source of natural aromatic compounds, accounts for almost 25% of the total biomass and has great potential for producing value-added chemicals and biofuels.^{2,3} The paper and pulp industries produce and extract more than 50 million tons of alkali lignin each year, of which nearly 98% is consumed as low-value fuel and emits hundreds of tons of greenhouse gases.⁴ Therefore, it is of particular importance to improve the efficient economy of alkali lignin.

Lignin is composed of a complex three-dimensional crosslinked structure, and its molecule contains a variety of functional groups, including aliphatic hydroxyl, phenolic hydroxyl, methoxy, and so forth.⁵ The strong bond energy of lignin results from two main linkages of C–C bonds and C–O bonds, which account for more than 56% of the total bonds.⁶ Consequently, it makes the lignin depolymerization (LDP) process extremely challenging. At present, the methods of lignin depolymerization can be divided into thermochemical treatment, mechanical treatment, biological treatment, electrochemical treatment, and so forth.^{7,8} Among them, thermochemical methods enable efficient lignin depolymerization, including rapid pyrolysis, microwave-assisted pyrolysis, depolymerization of oxidized lignin, ionic liquid-assisted catalysis, subcritical or supercritical fluid-assisted catalysis, and other types of catalysis.^{8,9} Furthermore, metal-catalyzed lignin depolymerization is one of the most popular methods to convert lignin into value-added chemicals. Although metalcatalyzed hydrogenolysis of lignin has been developed for many years, there is still a lack of efficient catalytic systems. Various catalysts based on precious metals or non-precious metals have been investigated in the literature.^{10,11} Ålthough noble metal catalysts (Pt, Pd, and Ru) show good catalytic activity and conversion efficiency, these low-abundance noble metal elements are not suitable as the main catalyst for largescale industrial applications. In addition, noble metal catalysts usually exhibit excessively ideal activity in the hydrogenation reaction of benzene rings, resulting in additional consumption

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of hydrogen, over-cracking of the benzene rings, and reduced yield of desirable aromatic chemicals.¹²⁻¹⁴ Therefore, transition metals (Ni, Mo, Fe) mainly belonging to VI, VIII, IX, and X groups are widely explored as the catalysts for lignin depolymerization. Many researchers have studied the catalytic depolymerization of lignin using catalysts with different metals and carriers. Compared with single-metal catalysts, bimetallic and bifunctional catalysts have received growing attention in recent years due to their multiple active sites and excellent catalytic activity. Ni, as a very common metal catalyst, has demonstrated good catalytic activity for the depolymerization of lignin; $^{15-17}$ MoO₃ and β -Mo₂C have high activity and selectivity for the cleavage of phenolic Ph-O-Me bonds and aliphatic Ph–O–Me bonds.^{18–20} Compared with mono-metal catalysts, the synergistic effect of Ni-Mo bimetallic catalysts can promote the depolymerization of lignin. Moreover, the study of the mechanism of synergy shows that there are three main factors: (1) increase the surface metal active sites; (2)increase the reactivity of H_2 and the substrates; and (3) hinder the further hydrogenation of the benzene ring.^{16,21} The introduction of the second metal has the potential to increase the catalytic activity, catalyst stability, and change selectivity due to its geometric, electronic, synergistic, and bifunctional effects.²² Li et al.²³ found that the Ni-W₂C catalyst with carbon as a carrier could decompose lignin into monophenols through hydrogenolysis with a yield of 46.5 wt %, while neither Ni/AC nor W2C/AC can produce monophenols higher than 20 wt %. Their work demonstrated a better catalytic performance of bimetallic catalysts in liquid-phase lignin conversion.

Meanwhile, due to its distinctive structure and cheap and abundant properties, lignin is considered as a promising carbon-based carrier. It is used to prepare catalysts in various forms such as supported, embedded, and nanosphere structures, as well as functional carbon materials such as supercapacitors and heavy metal adsorbents.²⁴⁻²⁹ Due to its oxygen-containing functional group, the lignin-based catalyst can embed the metal in the substrate by reaction. This kind of embedded catalyst, in which metal nanoparticles are inserted or partially embedded in mesoporous or microporous materials, is attractive to prevent metal aggregation. The surface functional groups of lignin-based catalysts, including carboxyl groups, have interesting catalytic properties, including absorption of substrates, and have been used as catalysts for many chemical reactions.³⁰ Zazo and his colleagues reported a catalyst of activated carbon-supported iron nanoparticles which was synthesized via FeCl3 activated lignin at 800 °C and used for phenol-catalyzed wet peroxide oxidation (CWPO). The synthesized catalyst showed quite good catalytic activity and very high stability, and there is almost no iron leaching under the reaction conditions.³¹ Yan et al. reported a simple in situ approach for preparing FeNPs encapsulated in charcoal by heat-treating the lignin-rich woody biomass. The catalysts were applied to convert synthetic gas into liquid fuel and presented good catalytic activity and selectivity to liquid hydrocarbons.³² By embedding Ni nanoparticles in lignin-derived carbon, Wang et al. constructed an "embedded" catalyst Ni/C-I to improve the stability of lignin depolymerization catalysts and regulate the metal-support interaction. Compared with the traditional "supported" Ni/C, the catalytic performance of lignin depolymerization was better, and the yields of aromatic monomers and bio-oil reached 23.3% and 82.4%, respectively.³³ Yu et al. proposed a novel orthogonal-type α -Mo₂C-

based catalyst using biomass in situ pyrolysis products as the carbon source and support. Pine- Mo_2C catalysts enhanced bond breaking and deoxidation of lignin pyrolysis vapor under ambient pressure, and the yield of monocyclic aromatic hydrocarbons was 13.26 wt %, of which aromatic hydrocarbons with a side chain accounted for 74%.³⁴

Catalysts can reduce the activation energy of chemical bonds and use H* to break the complex and highly polymerized structure of lignin. High value-added chemicals such as low molecular weight hydrocarbon fuels and phenolic product can be obtained through hydrodepolymerization of lignins. According to the source of hydrogen, the depolymerization reaction is divided into in situ and ex situ. The methoxy and other groups of the side chain of benzene ring of lignin molecules are selectively cleaved to generate phenol products through hydrogenation or hydrogenolysis. The condensation of intermediates into oligomers is a crucial issue, and the repolymerization of reaction intermediates into an oligomer or a solid product is also a limiting factor for lignin depolymerization.³⁵ 1,4-Dioxane has been reported to be able to inhibit the condensation of the monomers into oligomers during LDP.36 Methanol and water reforming system can provide H* for the depolymerization of lignins to help break the chemical bond of the lignin skeleton. The 1,4dioxane oxidation system can inhibit the formation of byproducts and improve the depolymerization efficiency of lignin. The combination of methanol and water reforming system and 1,4-dioxane could improve the depolymerization effect of lignins.³⁷

In this paper, lignin is used as a carbon source to prepare an embedded bimetallic catalyst (Ni–Mo/C_{-WMO}) for catalytic liquid-phase depolymerization of lignins. The catalysts were synthesized by wet and melt impregnation and air oxidation treatment, and other physical and chemical modification methods to achieve the directional regulation of Ni, MoO₃, and Mo₂C metal lattices. A high lignin depolymerization effect was obtained to realize the efficient utilization of lignin. A series of characterization techniques were carried out to study the physicochemical properties of the catalysts to explore the catalytic effects of different preparation methods of carbon-based catalysts on LDP. The influence of solvent systems (including external hydrogen source and in situ hydrogen production) was also investigated to optimize the LDP process.

2. MATERIALS AND METHODS

2.1. Materials. All chemical reagents in this study were analytical grade and were used without further purification. Alkali lignin, phenol (99.5%, GC), guaiacol (99.5%, GC), creosol (98.0%, GC), 2-methoxy-4-ethyl phenol (98%+), and tetrahydrofuran (99.0%, AR) were purchased from Shanghai Titan Technology Co., Ltd., China. Nickel nitrate hexahydrate (98%, AR) was obtained from Beijing Enokai Technology Co., Ltd., China. 1,4-Dioxane (>99.0%, AR), ammonium molybdate (99.5%, AR), and methanol (99.9%) were supplied by Sinopharm Chemical Reagent Co., Ltd., China. 2-Methoxy-4-propyl phenol (98%) was bought from Qiaoyi Biotechnology (Shanghai) Co., China. Ethyl acetate (>99.0%, GC) and ethanol (99.5%, AR) were purchased from Aladdin (Shanghai, China). Deionized water was made by a laboratory pure water system (Master Tourch-S15UV, Shanghai Hetai Instrument Co., Ltd., China).

2.2. Catalyst Preparation. Lignin was employed as a catalyst substrate and carbon source, and Mo and Ni were loaded or embedded on the lignin. The carbon chain of lignin was used as the template of catalyst to construct mesoporous and microporous

structures. The catalysts synthesized by the incipient wetness impregnation method, melt impregnation method, hydrothermal method, incipient wet-melt impregnation method, incipient wetness impregnation with oxidation method, wet-melt impregnation method, and wet-melt impregnation with oxidation method are denoted as Ni-Mo/C-_{TW}, Ni-Mo/C-_M, Ni-Mo/C-_H, Ni-Mo/C-_{TWM}, Ni-Mo/C-_{TWO}, Ni-Mo/C-_{WMO}, respectively. Specific synthesis methods were described in the Supporting Information (Scheme S1).

The Ni-Mo/C-WMO catalyst was synthesized as follows: alkali lignin was dried at 105 °C for 24 h to remove the moisture content. The total metal loading was designed to be 15 wt % with a molar ratio of Mo to Ni equal to 1:1. The mixture was stirred in a water bath at 65 °C with 80 RPM for 4 h. After stirring, the solid-liquid mixture was transferred to a centrifuge (5804R, Eppendorf, China), and the centrifuged solid sample was washed with deionized water and ethanol twice separately to remove the impurities such as inorganic salts. After that, the solid samples were dried in a vacuum drying oven (DZF-6050, Shanghai Yiheng Scientific Instrument Co., Ltd., China) at 65 °C for 9 h. The dried solid was taken out, ground, and put into the tube furnace (OTF-1200X ϕ 100, Hefei Kejing Material Technology Co., Ltd., China) for pyrolysis. The temperature was first set to 60 °C and then increased to 200 °C and held for 2 h and then pyrolyzed at 600 $^\circ\text{C}$ for 4 h in N_2 atmosphere. After pyrolysis, the catalyst was calcined in the air at 400 °C for 4 h to remove the solid residue on the surface. Then, it was reduced under 10% H_2/N_2 atmosphere at 600 $^\circ\mathrm{C}$ for 4 h. Finally, the sample was passivated in a 0.1% O_2/N_2 atmosphere and cooled to room temperature. The prepared Ni-Mo/C-WMO catalyst was preserved under N2 atmosphere in a sample tube.

2.3. Catalyst Characterization. The characterizations of the catalysts were all carried out in the Analysis and Testing Center of Shanghai Jiao Tong University. X-ray diffraction (XRD, Bruker D8 DaVinci X-ray diffractometer using Cu K α 1 radiation with a wavelength of 1.540598 Å) was performed to analyze the crystal phases of samples. The XRD patterns were collected within the 2θ range of 5^{-90°}. The surface morphologies and particle sizes of Mo/ Ni-C catalysts were examined by a scanning electron microscope (SEM-EDS). The SEM instrument used was Gemini 300, ZEISS, Germany, with a resolution of 0.6 nm @15 kV, an amplification factor of 10-1,000,000×, and an acceleration voltage adjustment range of 0.02-30 kV. The EDS instrument was INCA X-Act, Oxford. Textural properties were investigated by nitrogen adsorption-desorption isotherms conducted on the Quantachrome, Autosorb-iQ3. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area, while the Barrett-Joyner-Halenda (BJH) method was used to determine porosity (pore size, pore volume). The contents of Ni and Mo in the catalyst were determined by an inductively coupled plasma atomic emission spectrometer performed on an AGILENT ICP-OES 730 spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out on the ESCALAB 250xi equipped with a monochromated Al Ka X-ray source (hv = 1486.6 eV, 15 kV, 10.8 mA). The binding energies were calibrated using a criterion of a C^1 peak (284.8 eV) as a reference.

2.4. Lignin Depolymerization Experiments. 0.20 g of lignin, 0.10 g of catalyst, and 20 mL (25 mL) of solvent were added to the 50 mL autoclave reactor [YZPR-50, Jiwu (Shanghai) Environmental Protection Equipment Co., Ltd., China]. The reactor was purged with N₂ (H₂) for 5 times. Then, the initial pressure was increased to 3.0 MPa before heating the reactor. Finally, the reaction was conducted at 260 °C for 4 h. After the reaction, the reactor was cooled to room temperature with an ice water bath.

The gaseous products, CO, CO₂, CH₄, C₂H₆, and C₂H₄, were quantified by gas chromatography [GC, Agilent 7890 (FID–GS–Gaspro, 113–4362(60 m × 0.320 mm × 0 mm)]. Since the yields of these gaseous products were too small (less than 1 wt %) and we focus on the liquid and solid product in this study, gaseous products were not further analyzed. The solid–liquid mixture was filtered through a 0.45 μ m filter membrane. The solids on the membrane consisted of unreacted lignin, catalyst, and char. The collected solids

were washed with ethyl acetate (EA) and water consecutively. Monophenols were collected as the liquid product by EA extraction, while lignin oligomers resided in the water phase. The monomer product was analyzed by GC–MS (Agilent 7890 GC and Agilent 5977B mass selective detector). Guaiacol was used as an external standard, and the reaction factors of other major phenolic products (phenol, creosol, 2-methoxy-4-ethyl phenol, and 2-methoxy-4-propyl phenol) were quantitatively analyzed by GC–MS to obtain the yields. The response factors of five major phenolic products and detailed experimental procedures are presented in Supporting Information (Scheme S2).

The conversion of lignin was obtained from the weight of unconverted and original lignins, as shown in eq 1. Through the GC–MS results, the liquid yield is shown in eq 2, the lignin oligomer yield is shown in eq 3, and the char yield is shown in eq 4. The mass balance of the whole experiment is presented by eq 5.

$$C_{\rm L} \,({\rm wt}\,\%) = \frac{M_{\rm L} - M_{\rm THF}}{M_{\rm L}} \times 100\%$$
 (1)

$$Y_{\text{liquid}} (\text{wt \%}) = \frac{M_{\text{liquid}}}{M_{\text{L}}} \times 100\%$$
(2)

$$Y_{\rm O} ({\rm wt} \%) = \frac{M_{\rm O}}{M_{\rm L}} \times 100\%$$
 (3)

$$Y_{\rm char} (\rm wt \%) = \frac{M_{\rm char}}{M_{\rm L}} \times 100\%$$
(4)

$$M_{\rm b} = \frac{(M_{\rm liquid} + M_{\rm O} + M_{\rm char} + M_{\rm THF})}{M_{\rm L}} \times 100\%$$
(5)

 $M_{\rm L}$ is the weight of the original lignin, $M_{\rm THF}$ is the lignin dissolved in tetrahydrofuran, and $C_{\rm L}$ is the conversion rate of lignin. $M_{\rm liquid}$ and $Y_{\rm liquid}$ are the weight and yield of the monophenols, respectively, while $M_{\rm O}$ and $Y_{\rm O}$ are the weight and yield of oligomers. $M_{\rm char}$ is the weight of char and $Y_{\rm char}$ is the yield of char. $M_{\rm b}$ is the overall mass balance from each experiment.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization. The three preparation methods including hydrothermal carbonization (Ni–Mo/ C_{-H}), incipient wetness impregnation (Ni–Mo/ C_{-IW}), and melt impregnation (Ni–Mo/ C_{-M}) were compared to illustrate their effects toward LDP. The textural properties of Ni–Mo/ C_{-H} , Ni–Mo/ C_{-IW} , Ni–Mo/ C_{-M} , and char are shown in Table 1. The char sample (synthesized by pyrolyzing lignin at 600 °C in N₂ atmosphere without other improvements) exhibits the second smallest surface area (2.6 m²/g) and the smallest total pore volume without micropores. The poor porous structure of the catalyst is fatal in heterogeneous catalytic systems as it

 Table 1. Textural Properties of Catalysts Prepared via Three

 Methods

samples	$S_{\rm BET} (m^2/g)$	$\frac{V_{\text{total}}^{a}}{(\text{cm}^{3}/\text{g})}$	$V_{\rm meso}^{\ b}$ (cm ³ /g)	$\frac{V_{\text{micro}}}{(\text{cm}^3/\text{g})}$	R ^d (nm)
carbon ^e	2.6	0.003	0.003		4.81
Ni-Mo/C- _H	20.0	0.014	0.006	0.008	2.90
Ni-Mo/C _{-IW}	427.9	0.73	0.25	0.48	6.79
Ni-Mo/C _{-M}	0.6	0.013	0.009	0.004	84.71
Ni-Mo/C _{-WMO}	338.5	0.23	0.093	0.13	2.68

^{*a*}Total pore volume. ^{*b*}Mesopore volume obtained by the BJH method. ^{*c*}Micropore volume by the SF method. ^{*d*}Average pore diameter obtained by the BJH method. ^{*e*}Derived from lignin pyrolyzed at 600 °C in N₂ atmosphere.

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Figure 1. (a) XRD patterns of Ni–Mo/C-_H (hydrocarbon), Ni–Mo/C-_{TW} (incipient wetness impregnation), Ni–Mo/C-_M (melt impregnation), and Ni–Mo/C-_{WMO} (wet-melt impregnation with oxidation method); (b) XPS spectrum of Mo 3d of Ni–Mo/C-_{WMO}; (c) XPS spectrum of Ni 2p of Ni–Mo/C-_{WMO}.

prevents the catalyst from contacting with the substrate and attaching active H* species to active sites for subsequent reactions. Similarly, the Ni-Mo/C-H catalyst from hydrothermal carbonization and Ni–Mo/C- $_{\rm M}$ from melt impregnation also show small specific surface area and total pore volume. The specific surface area of the Ni-Mo/C-M catalyst $(0.6 \text{ m}^2/\text{g})$ is lower than that of char without any treatment. The melting metal precursors occupy the pores of the lignin substrate and decrease the specific surface area of the synthesized catalyst. In addition, the pore size distribution of the Ni-Mo/C-_M catalyst exhibits the most pore concentrate at around 2.20 nm, but the larger pores of 146.98 nm result in a higher average pore size of 84.71 nm. In contrast, Ni-Mo/ C-IW catalyst from the incipient wetness impregnation method has a higher specific surface area (427.9 m^2/g), which is beneficial for the contact between active sites and reactants. Ni-Mo/C-IW is more likely to show better catalytic performance in the lignin depolymerization experiment.

As shown in Figure 1a, the catalyst obtained by the incipient wetness impregnation Ni–Mo/C-_{IW} and hydrothermal carbonization method Ni–Mo/C-_H can only obtain the crystal lattice of Ni without obviously observing the corresponding active components of Mo. Ni–Mo/C-_M illustrates more crystal lattice types, such as Ni, β -Mo₂C, and MoO₃, than the other two catalysts without considering the influence of the specific surface area. It has more metal lattices, and the synergistic effect of Ni-Mo bimetal can facilitate the bond-breaking performance in the complex reaction of lignin depolymerization. The comparison of three catalysts indicates that the higher specific surface area of Ni-Mo/C-IW is beneficial to the adsorption of lignins or monomers in the reaction during lignin depolymerization, and the catalyst Ni-Mo/C-M prepared from the melt impregnation method displays more crystal lattices, which can play a better synergistic role in the face of complex reactions. Among the various crystal lattices in the Ni-Mo/ C-M catalyst, it is more desirable to obtain metal lattices such as MoO₃ and β -Mo₂C that result in good catalytic effects for liquid-phase lignin depolymerization. Meanwhile, it was reported that the air oxidation treatment can eliminate the carbon deposition on the catalyst surface during pyrolysis, increasing the specific surface area of the catalyst and exposing more active sites.³³ Therefore, we explore a new type of catalyst Ni-Mo/C-wmo in order to get higher specific surface area and more active sites by the wet impregnation method combined with the melting impregnation and oxidation treatment.

Table 1 shows that the improved Ni-Mo/C-_{WMO} catalyst has a relatively large specific surface area of 338.506 m²/g,

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entry	catalyst	CL (%)	YL (%)	1	2	3	4	5	others	YO (%)	YC (%)	$M_{\rm b}~(\%)$
1	Ni-Mo/C-IW	62.37	10.26	1.31	26.80	40.87	8.31	2.15	24.02	43.04	8.42	99.35
2	Ni-Mo/C-M	56.64	8.28	1.03	20.73	36.39	9.42	3.72	28.43	39.29	8.64	99.57
3	Ni-Mo/C-IWM	68.73	11.91	2.21	65.70	12.40	5.74	1.46	12.50	47.63	8.32	99.13
4	Ni-Mo/C- _{WM}	74.62	16.72	2.41	71.50	9.13	5.15	1.31	10.47	49.57	7.66	99.33
5	Ni-Mo/C- _{IWO}	80.64	16.89	1.82	70.91	10.74	5.03	1.08	10.43	55.00	6.30	97.55
6	Ni-Mo/C- _{WMO}	87.62	42.45	1.29	26.83	40.75	8.22	2.60	20.30	33.92	6.67	95.42

"Reaction condition: 0.2 g alkali lignin, 0.1 g catalyst, 5 mL deionized water + 15 mL methanol, 3 MPa N₂, 4 h, 260 °C, stirring at 1000 rpm. ^bThe selectivity of the 5 main phenolic products and another selectivity. 1 is phenol, 2 is guaiacol, 3 is creosol, 4 is 2-methoxy-4-ethyl phenol, and 5 is 2-methoxy-4-propyl phenol.



Figure 2. Yield and conversion of lignin depolymerization under Ni–Mo catalysts treated by different methods. (a-c) Comparison of individual modification methods. (d) Comparison of all the prepared catalysts.

which improves the adsorption capacity of the catalyst to the substrate. As shown in Figure 1a, four obvious diffraction peaks corresponding to MoO_3 (060), Ni(111), Ni(200), and Ni(220) can be observed over the Ni–Mo/C-_{WMO} catalyst. Figure 1b demonstrates that Mo exists in the form of Mo^{6+} (MoO_3) and Mo^{2+} (Mo_2C), which is consistent with the results of Karthick's work.⁴⁰ Figure 1c shows that Ni exists in the form of Ni⁰⁺ and Ni²⁺. This proves that the Ni–Mo/C-_{WMO} catalyst contains Ni, β -Mo₂C, and MoO₃ active species

to improve the breaking C–O and C–C bonds during LDP. The SEM results of Figure S1 (Supporting Information) show that the metal particles supported on the carbon-based surface exist in two forms. One is the metal supported on the carbon-based material (a, b), and the other is a metal alloy or a cluster which grows between the pores and slits of the carbon-based material (c, d, e). The loaded metal is proved to be well dispersed on the lignin substrate, and the crystal lattices grown on the support display a shape of a cubic unit cell. It indicates

Table 3. Effects of Different Solvent	ystems on the Depo	lymerization of Lignins ^e
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					mo	nophenols						
entry	solvent systems	C _L (%)	$Y_{\rm L}$ (%)	1	2	3	4	5	others	Y ₀ (%)	Y _C (%)	$M_{ m b}$ (%)
1 ^c	20 mL deionized water	82.26	26.39	0.87	51.57	7.04	1.96	0.57	37.98	49.93	3.94	98.01
2	5 mL water + 15 mL methanol	87.62	42.45	1.29	26.83	40.75	8.22	2.6	20.3	33.92	6.67	95.42
3	5 mL water + 15 mL isopropanol	88.78	15.5	1.11	63.97	17.9	10.03	2.89	4.09	60.65	10.57	97.94
4 ^{<i>c</i>}	20 mL 1,4-dioxane	89.2	23.43	1.29	13.8	32.3	20.7	13.3	18.61	52.62	9.3	96.15
5	5 mL water + 15 mL methanol + 5 mL 1,4-dioxane-1	99.82	62.95	0.12	12.4	40.85	36.42	2.34	7.88	31.4	4.97	99.5
6 ^{<i>d</i>}	5 mL water + 15 mL methanol + 5 mL 1,4-dioxane-2	96.49	38.75	0.2	21.78	40.36	28.11	3.65	5.9	55.7	1.42	99.38

^{*a*}Reaction conditions: 0.2 g alkali lignin, 0.1 g Ni–Mo/C-_{WMO} catalyst, 3 MPa N₂, 4 h, 260 °C, stirring at 1000 rpm. ^{*b*}The selectivity of the 5 main phenolic products and another selectivity. 1 is phenol, 2 is guaiacol, 3 is creosol, 4 is 2-methoxy-4-ethyl phenol, and 5 is 2-methoxy-4-propyl phenol. ^{*c*}This reaction was under 3 MPa H₂. ^{*d*}This reaction was under 1 MPa N₂.

that Ni–Mo/C- $_{WMO}$ has a better microscopic morphology and crystal lattice and displays exceptional catalytic activity in LDP. The experiments of LDP to produce phenolic products using the above catalysts in water and methanol system were carried out to verify the catalytic effect of the Ni–Mo/C- $_{WMO}$ catalyst.

3.2. Lignin Depolymerization. 3.2.1. Catalytic Performance. The lignin depolymerization performance with various catalysts is displayed in Table 2 and Figure 2. The liquid yield of 10.26% is achieved by the incipient wetness impregnated catalyst Ni-Mo/C-IW, while 8.28% is reached by the melt impregnated catalyst Ni-Mo/C-M. Neither catalyst displays very high catalytic performance in LDP, which is consistent with the catalyst characterization results. For the incipient wetness impregnated catalyst Ni-Mo/C-IW, although it has a large specific surface area, it lacks effective and active sites of Mo for the catalytic reaction. This kind of embedded catalyst is not very different from the catalysts that support the metal only with nickel, and the advantages of bimetallic catalysts are not fully realized due to the lack of molybdenum lattice. For the melt-impregnated catalyst Ni-Mo/C-M, although it has a wider variety of active sites, the reactants are still difficult to adsorb on effective active sites to participate in catalytic reactions due to its low specific surface area. So only 56.64% of lignin participates in this reaction. The catalytic activity of the catalysts can be improved after modifications.

As illustrated in Figure 2a, compared with Ni-Mo/C-TW (10.26%) and Ni–Mo/C- $_{\rm M}$ (8.28%) catalysts, the monophenol yield from Ni-Mo/C-_{IWM} increases to 11.91% as this catalyst initially combines the advantages of the two methods and shows distinct reactivity with a larger specific surface area. Figure 2b exhibits that the liquid yield is further enhanced to 16.72% from the wet-melt impregnation compared with 11.91% from the incipient wetness-melt impregnation. The effectiveness of lignin depolymerization can be attributed to multi-active sites of Ni-Mo/C-WM. Although the incipient wetness impregnation can avoid the loss of metal loading content, the uneven dispersion of metal in the aqueous phase leads to metal agglomeration and less metal active sites, which inhabits the catalytic activity of the catalyst and leads to the poor depolymerization effect of lignins. While the wet impregnation only retains the metal embedded in the catalyst substrate during stirring, leading to better metal dispersibility, which can reduce metal agglomeration and increase the effective active sites. However, the loading content is lower than that designed due to the filtration process. In the Ni-Mo/C-WMO catalyst, the loads of Ni and Mo are quantified to be 7.58 and 2.13 wt % as shown in Table S2 (Supporting

Information). Figure 2c shows that after the oxidation treatment of the incipient wetness impregnation catalyst, the liquid yield of the lignin depolymerization increases from 10.26 to 16.89%. This improved catalytic activity can be attributed to removing the coke covering the metal sites by oxidation³³ Therefore, the new catalyst Ni-Mo/C-WMO, obtained by combining the above-mentioned modification methods for the incipient wetness impregnation catalyst, has higher catalytic activity. This Ni-Mo/C-WMO catalyst increases the liquid yield of lignin depolymerization to 42.45% under the in situ hydrogen production system of water and methanol. The reason is that it has a higher specific surface area and effective active sites of MoO₃, Mo₂C, and Ni. At the same time, due to the bifunctional effect of the lignin-based catalyst and the interaction between the substrate and the active sites, the catalyst is more likely to break the C–O bond in lignins. Figure 2d shows that through continuous modification, Ni-Mo/ C-WMO can make 87.62% lignin participate in the reaction and selectively improve liquid products in the lignin depolymerization experiment, and the formation of oligomers is greatly inhibited. Compared with other catalysts, cresol has the highest selectivity in liquid yield, reaching 40.75%. This is due to the presence of a large number of MoO₃ and Mo₂C active sites which enhance the utilization of active H* to break C-C and C-O bonds, resulting in a higher liquid yield and lower oligomer yield.

For the in situ hydrogen production reaction system, the catalyst is not only selective for lignin depolymerization and cleavage of β -O-4, 4-O-5, and C-C bonds but also catalyzes the reforming reaction of methanol and water to produce H₂. Kozyatnyk et al.⁴¹ found that the lignin substrate, compared with other supports such as Al₂O₃, SiO₂, and HZSM-5, exhibit very high hydrogen production capacity under the methanol-reforming system. We can preliminarily judge lignin-based catalysts to have a good dual function in the in situ hydrogen production system. The solvent reforming for hydrogen production and lignin depolymerization reaction can both be catalyzed via the well-prepared Ni-Mo/C-_{WMO} catalyst in this work.

3.2.2. Influence of the Solvent System. The results of lignin depolymerization under different solvent systems are shown in Table 3. The effects of the in situ hydrogen system and external hydrogen system to achieve lignin depolymerization are similar in entries 1 and 2. Compared with the external hydrogen system, the in situ hydrogen system with methanol and water can produce higher phenolic yield. Due to the presence of alcohol in the system, the intermediate products of



Figure 3. Yield and conversion of lignin depolymerization under different solvents with the Ni $-Mo/C_{WMO}$ catalyst. (a) Comparison of in situ and ex situ hydrogen systems. (b) Advantages of the three-solvent system. (c) Different pressures in the three-solvent system. (d) Comparison of all the solvent systems.

the reaction prone to dissolve in the alcohol phase, absorbed by the catalyst as the alcohol phase moves, and the reaction intermediate facilitate subsequent reactions to increase the yield of phenolic products. By comparing entries 2 and 3, it can be seen that the yield of monophenol is higher in the water and methanol system as a result of the effect that reforming isopropanol and water to hydrogen is not as effective as methanol and water. A small amount of active H* produced by reforming isopropanol and water can only depolymerize macromolecules of lignins into oligomers, and it is difficult to further depolymerize oligomers into monophenol. As a result, the depolymerization products of lignins in this system were mainly oligomers (60.65%). A small amount of hydrogen can only break the more easily broken β -O-4 bond during the reaction, so its effect of lignin depolymerization is less than in the methanol and water system. As a dual solvent system, the methanol and water system enhances hydrogen production and its further participation in C-O and C-C bond breaking of oligomers to monomers, thus increasing the monophenol

products of LDP. This experiment result also agrees well with Ma's conclusion. $^{\rm 42}$

Figure 3a shows that the methanol and water system yields 42.45% monophenols, higher than that from individual water system and water—isopropanol system, indicating an efficient lignin depolymerization. It can be seen that the conversion of lignins under the dual solvent system reaches more than 60%. Creosol is the major product under the methanol and water system, while guaiacol is the main product under the external hydrogen system. There was no significant difference in the yield of guaiacol between the two systems using different hydrogen sources, but the yield of creosol was significantly increased in the methanol and water system. This is mainly because it is difficult for the intermediates to contact with the catalyst in the aqueous phase, while in the alcohol phase, the oligomer can further react to break its linkages to produce monophenols such as creosol with the aid of catalysts.

It can be observed that the yield of undesirable oligomers is still high, and it is necessary for the conversion of oligomers



Figure 4. Liquid product selectivity in different solvent systems with the Ni-Mo/C-_{WMO} catalyst.

into monophenols. 1,4-Dioxane has been used as a solvent and has shown the ability to reduce the repolymerization of lignins.^{39,43,44} It can oxidize the reactive intermediates produced in the reaction, thereby inhibiting the recondensation of monomers. Therefore, the combination of in situ hydrogen production and 1,4-dioxane can lead to an improvement in the performance of LDP and suppress the recondensation of reaction intermediates. As shown in Figure 3b, the mixed-solvent system composed of methanol and water reforming for hydrogen production coupled with 1,4-dioxane shows a 99.82% conversion of lignin. In this system, the use of 1,4-dioxane not only improves the lignin conversion and liquid yield but also reduces the oligomer and char yield. At the same time, the yield of char is the highest in the pure 1,4-dioxane system, because the water phase can make the catalyst more stable and reduce the dehydration and condensation reaction of intermediate oligomers on the catalyst surface to form char. As shown in Figure 3c, when N_2 pressure is reduced from 3 MPa (water + methanol + dioxane-1) to 1 MPa (water + methanol + dioxane-2), the liquid yield decreases, the oligomer content increases, and the char content goes down. The decrease of N₂ pressure probably reduces the collision of active H* and the reactants, and the input energy is insufficient to break C-C and C-O bonds. Meanwhile, the produced intermediate oligomers do not undergo dehydration condensation or other reactions on the catalyst surface to form char. However, we can notice that in the mixed-solvent system, LDP can still maintain a high lignin conversion, which makes lignins more effectively depolymerized into the target product. In the mixed-solvent system of methanol, water, and 1,4dioxane, the mixture of methanol and water can be reformed to produce hydrogen and increase the H* of the system, while 1,4-dioxane can increase the polarity of the solvent and inhibit the recondensation of reaction intermediates to form oligomers.

The results suggest that the synergistic effect of the threesolvent system facilitates the depolymerization of lignins into phenolic products. Moreover, the directional selectivity of creosol (40.85%) and 2-methoxy-4-ethyl phenol (36.42%) reached as high as 77.27%. From Figure 4, it can be seen that the yield of LDP reaction in the water phase and other dual solvent systems is very high because H* can convert complex functional groups into a phenolic hydroxyl group. Meanwhile, in the water phase and external hydrogen systems, excessive H* also break the C–C bond in creosol, 2-methoxy-4-ethyl phenol, and 2-methoxy-4-propyl phenol, thus transforming them into guaiacol. However, creosol and 2-methoxy-4-ethyl phenol are the major products in the three-solvent system, because the presence of dioxane made the C_β-OH bond in the reaction oxidized to C_{β} =O bond, and the free active H* is more inclined to break C_{α} =O bond than C–C bond located on carbon 4, which improves the selectivity of the two products to some extent.

3.3. Evolution of Functional Groups during Lignin Depolymerization. The liquid-phase product analysis of the lignin depolymerization experiments indicates that the monophenolic compounds are the major liquid products. To more intuitively analyze the complex lignin structure, 2D HSQC NMR analysis was performed on the original lignin and lignin oligomer, which was the reactive residual collected from the experiment of the Ni-Mo/C-WMO catalyst in the three-solvent system. According to the results in Figure 5, each 2D HSQC NMR spectrum consists of three regions: the saturated aliphatic region ($\delta_{\rm C}/\delta_{\rm H}$ = 10–50/0.5–3.0 ppm), the oxygenated region ($\delta_{\rm C}/\delta_{\rm H}$ = 45–90/2.5–5.0 ppm), and the aromatic region ($\delta_{\rm C}/\delta_{\rm H}$ = 105–135/6.0–7.6 ppm). After the catalytic depolymerization process, the intensity of the aromatic signal is significantly reduced, the oxygen-containing side-chain region is slightly decreased, and the signal intensity of the aliphatic side-chain region is significantly increased. For the oxygenated region, the obvious signals of β -O-4 bond (A), the pinoresinol $(\beta - \beta)$ linkages (C), and methoxy structure (OMe) could be observed in lignins in Figure 5 (left). The H, G, S, FA, PB, and pCA units could be detected in the aromatic region for raw lignin. For the oligomer in Figure 6 (right), in the oxygenated region, the obvious signals of β -O-4 bond (A), the pinoresinol (β - β) linkages (C), and methoxy structure (OMe) are reduced. In the aromatic region, the FA, PB, S, and H units could barely be detected for the oligomer. Meanwhile, the signals of S, G, and pCA show a significant decline. The β -O-4 bond in lignins can be easily destroyed by metal-catalyzed LDPs. The disappearance of the



Figure 5. 2D HSQC NMR spectra of raw lignin (left) and oligomer after reaction (right).

 $\beta-\beta$ bond and α -O-4 bond in the oligomer further indicates that the catalyst has a positive effect on the depolymerization of lignins. It is worth noting that the corresponding structural region of H and other units of lignins disappeared after the reaction, indicating that such units have higher reactivity and are more prone to fracture and transform during the reaction process. In addition, it can be seen that the signal of the aliphatic region of the oligomer is remarkably increased compared with that of the original lignin. Many new peaks corresponding to bonds between methyl and ethyl groups and aromatic rings are observed. This is probably because lignin undergoes esterification, O-alkylation (alkylation on the –OH group of phenols), C-alkylation (alkane on the aromatic ring group), methylation, and ethylation reactions during the catalytic depolymerization of lignins. By breaking β –O–4, β – β , α –O–4, and other bonds, which make up the complex structure of lignins, lignins can be transformed into monophenol and other structures. The results demonstrated that the β –O–4 bonds in the lignin are effectively destroyed and the liquid yield increases within the three-solvent systems and the hydrogenolysis process using Ni–Mo/C-_{WMO}.

3.4. Stability of the Optimized Catalyst. The catalytic activity and stability of catalysts are very important indicators to evaluate their performance in heterogeneous reactions. Due to the special structure and abundant active sites of catalysts, they play an excellent catalytic performance in liquid-phase lignin depolymerization as described previously. On the premise of good catalytic performance, the stability of catalysts should also be guaranteed. The stability of this type of embedded carbon-based catalysts has also been studied by



some researchers.^{33,45–47} In this study, the catalysts were stored and sealed up in the 5 mL sample bottle after purging N₂ to replace the air inside, thus preventing the oxidation and deactivation of the prepared bimetallic catalysts. However, the catalytic performance of the catalyst declines as time passes. This is attributed to the fact that high active sites such as Ni⁰ would react with O₂ and H₂O in the air and transform into oxide or hydroxide when exposed to some air.

As shown in Figure 6, the fresh Ni–Mo/C-_{WMO} catalyst, which was immediately applied in the lignin depolymerization experiments after preparation, exhibits the highest lignin conversion and liquid yield. However, the lignin conversion and liquid yield fell off significantly after the catalysts were stored for 9 and 15 days. After 15 days, the performance of the

Ni-Mo/C-_{WMO} catalyst remained stable, the lignin conversion was above 95%, and the liquid yield reached about 50%. (The Ni-Mo/C-WMO catalyst stored for 15 days depolymerized lignins with a conversion of 95.87% and a liquid yield of 52.87%, while the Ni-Mo/C-WMO catalyst stored for 17 days displayed a 96.13% lignin conversion and a 50.82% liquid yield.) The decline of the catalytic performance of catalysts stored for a long time can be because a part of the active sites is occupied by O* and OH* and prevents its contact with the intermediate products to catalyze the depolymerization of lignins more effectively. The catalysts can be hydrogenated again to reveal the active sites and the reduced catalyst (10% H_2/N_2 atmosphere at 600 °C for 4 h) is named refreshed catalyst. Through the lignin depolymerization experiment, we observe that the catalytic performance of the refreshed catalyst is improved with 98.28% lignin conversion and 58.92% liquid yield. This also indicates that even if the active sites of the catalyst are occupied by oxygen-containing substances, the Ni-Mo/C-WMO catalyst enables the catalytic desorption of oxygen-containing substances in the presence of H* and then continue to expose the active sites to participate in the reaction. The regeneration stability of the catalyst is very high, even stored in the air and other environments.

3.5. Proposed Reaction Pathway. According to the results of 2D-HSQC NMR and GC–MS, various reactions such as hydrogenolysis, dealkylation, demethoxylation, and dehydration may occur during the depolymerization of lignins, leading to the rupture of C–O and C–C bonds and further cracking of intermediate fragments of lignin. As a result, the lignin is depolymerized into various small molecular monophenolic compounds. Therefore, the possible pathway of lignin



Figure 7. Possible pathway of catalytic depolymerization reaction.

Article



Figure 8. Plausible reaction pathway for the formation of five major products.

depolymerization under this reaction system is proposed in Figure 7.

Under H₂ atmosphere from methanol and water reforming and with the Ni–Mo/C- $_{\rm WMO}$ catalyst, the $C_{\alpha}{-}OH$ group is etherified to break the C–O bond in C_{β} –O in the β –O–4 structure of lignin. At the same time, the hydrogen atom in C_{α} -OH can facilitate the cleavage of the C_{β} -O bond. In the depolymerization reaction, H₂ produced by methanol and water reforming dissociates in the system and generates active H*, which is adsorbed by MoO₃, Mo₂C, and Ni active sites. Active H* species adsorbed by the catalyst will hydrogenolyze and break the lignin structure when they contact with β -O-4 and C-O and C-C bonds of lignins to generate intermediate products. Active intermediates continue to react with free H* and attach to the catalytic sites for subsequent reactions such as dealkylation and demethoxylation and further transform into phenols. At the same time, the active intermediates also collide with each other, and the condensation reaction occurs. Due to the presence of 1,4-dioxane, it could oxidize the highly active $C\alpha$ -OH into $C\alpha$ =O, preventing recondensation between intermediates and thus reducing the formation of oligomers. This is also demonstrated by Luterbacher's work.³⁶ Meanwhile, the oligomers containing unsaturated bonds formed by polycondensation of some intermediates can be repolymerized into macromolecules and then form char by dehydration at the catalytic active sites. This also was confirmed in Wang's work.⁴⁸ Therefore, under the catalyst and three-solvent system, the β -O-4 and α -O-4 bonds of lignin were first broken to form structures similar to those in the 2D-NMR spectra, and then these structures were demethoxized and demethylated to form five main phenolic products.

In Figure 8, based on the products obtained during the catalyzed depolymerization of lignin, the potential reaction mechanism of C–C bond cracking may be can be divided into two main pathways: one is side-chain hydrogenation substitution; the other is side-chain oxidation substitution. We propose that in the first, second, and third structures, OH^+ radicals of other side chains or reaction intermediates of lignin initially attack the phenyl ring and the subsequent substitution of alkyl side chains leads to hydroxylation of the ring, resulting

in a substituted phenolic compound. In the fourth structure, the phenyl C_a -OH bond is oxidized to C_a =O bond by the oxidation of 1,4-dioxane, and hydrogen substitution reaction occurs to make it disappear into the phenolic structure. Due to the oxidation effect, the selectivity and yield of creosol and 2methoxyl-4-ethyl phenol are raised, while the selectivity of phenol and guaiacol decreases. In the fifth structure, C_{γ} undergoes hydrogen substitution to remove the oxygencontaining functional group and then break the $C_{\beta}-C_{\gamma}$ bond to get the corresponding product.

Through the analysis of mechanism and the above results of experiments, we can get some conclusions: at first, the hydrogenation of benzene and aliphatic C_{α} position to replace the hydroxyl hydrogen has inevitable competition, but in this work, the combined effect of the mixed-solvent system and Ni-Mo/C-WMO catalyst can effectively lead to completion of the selectivity of breaking of C-C, β -O-4, and α -O-5 bonds. At the same time, due to the presence of 1,4-dioxane, C_a -OH is oxidized to C_a =O bond in C-4 to produce the structure, which is subsequently hydrogenated to make $C_a = O$ into an alkyl structure under this solvent and the Ni-Mo/ C-WMO catalyst system. At the same time, compared with other studies in the literature, vanillin, the main product of alkali lignin depolymerization alone, was no longer present in this catalytic system. The spectral results of GC-MS are provided in the Supporting Information (Figure S3). It also indicated that the depolymerization of lignins was more complete and the types of depolymerization products were more uniform under the Ni-Mo/C-WMO catalyst and mixed-solvent system.

4. CONCLUSIONS

An efficient bimetallic Ni-Mo catalyst with active sites embedded on a carbon substrate was prepared using lignin as a carbon source. After modification, metal active sites such as Ni, MoO₃, and Mo₂C with excellent catalytic properties were obtained, and they played a significant role in the depolymerization of lignins. By comparing the preparation methods of various carbon-based catalysts, the suitable preparation and modification methods of carbon-based catalysts were proposed. The mixed-solvent system composed of water, methanol, and 1,4-dioxane also plays an effective role in promoting depolymerization with water and methanol reforming to produce hydrogen and 1,4-dioxane inhibiting polycondensation. The synergistic effect of multi-active sites of Ni-Mo/C-_{WMO} catalyst and mixed solvent results in the yield of mono-phenolic compounds reaching 62.95% under the conditions of 260 °C, 3MPa N₂, and 4 h reaction. The Ni-Mo/C-_{WMO} catalyst illustrates attractive bond-breaking ability of the C–C, β –O–4, α –O–5, and C=O bonds in lignins. Different from other catalysts and solvents in the previous literature, a large amount of vanillin and other structures generated in the depolymerization process of lignin can be further decomposed into monophenolic products in this work. The new design and synthesis strategy of bimetallic ligninbased catalysts exhibits excellent catalytic activity in lignin depolymerization reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.3c00063.

Preparation methods of various lignin-based catalysts in detail; experimental method of lignin depolymerization; SEM and ICP analyses of the Ni-Mo/C-WMO catalyst; retention time of different products from GC-MS; and GC-MS chromatogram of lignin depolymerization with the Ni-Mo/C-_{WMO} catalyst in different solvents (PDF)

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