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ARTICLE

In situ synthesis of molybdenum oxide @ N-doped Carbon from biomass for selective vapor phase hydrodeoxygenation of lignin-derived phenols under atmosphere H₂

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The vapor phase hydrodeoxygenation (HDO) of lignin-derived phenols under atmosphere H_2 has a great significance to produce high-quality fuels and commodity chemicals. Herein, we reported a simple, green method to prepare Molybdenum oxide @ N-doped carbon (MoOx@NC) via in situ pyrolysis of molybdenum precursor preloaded cellulose and demonstrated its catalytic performance on vapor phase HDO of lignin-derived phenols. When the pyrolysis temperature was at 600 °C, the catalyst (MoOx@NC-600) exhibited the best catalytic performance on vapor phase HDO of guaiacol. Through systematically investigating the parameters such as: reaction temperature, WHSV, residence time, and concentration, the optimal reaction conditions for vapor phase HDO of guaiacol was 450 °C, 1 h⁻¹ with atmospheric H₂. The concentration of the feed was 20% in mesitylene, and the residence time was about 3.3 s. The carbon yield of aromatic hydrocarbons was 83.3%, with 65.7% of benzene, 15.5% of toluene and 2.1% of alkylbenzenes. In addition, other lignin-derived phenols were also investigated and desired results were achieved with MoOx@NC-600 catalyst. Furthermore, MoOx@NC-600 showed good stability due to the N-doped carbon formed on the surface of the MoOx particles. The catalysts were characterized by elemental analysis, AAS, BET, XRD, XPS, TEM, and EDS mapping. The high catalytic performance of MoOx@NC-600 toward lignin-derived phenols HDO can be attributed to the synergistic effect of carbon supports and Mo⁵⁺ (molybdenum oxynitides), Mo^{δ +} (Mo₂N) and Mo⁴⁺ on the surface of MoOx particles.

1. Introduction

With the ultimate consumption of fossil resources and the emission of greenhouse gases, the study on alternative energy sources have got much attention. Lignocellulosic biomass is an attractive renewable feedstock that can be converted to the transportation fuels and chemicals.¹ Lignin, which comprises up to 30wt% of lignocellulosic biomass, is a natural polymer consisted of methoxylated phenylpropane units featuring numerous ether linkages (C-O-C), as well as hydroxyl (-OH), and methoxyl (-OMe) side groups.² Fast pyrolysis is an effective process that can convert lignin to generate a mixture of non-condensable liquid oil, gases, and solid.³ However, mono-phenols (such as phenol, syringol, guaiacol, and catechol), and other polysubstituted phenols in the lignin pyrolysis bio-oil lead to high instability, viscosity, corrosiveness, and polarity.^{4,5} Therefore, the oxygen must be removed before the lignin pyrolysis oil can be used as a substitute for diesel, gasoline or aromatic chemicals.

Hydrodeoxygenation (HDO) is the most promising route to improve the effective H/C ratio of pyrolysis bio-oils and produce hydrocarbons either as final fuel components (e.g., gasoline and diesel) or as fuel intermediates (small olefins and alkanes).^{6,7} The key challenge faced by HDO processes is achieving a high degree of oxygen removal, while reducing hydrogen consumption.⁸ Conventional hydrodesulphurization (HDS) / hydrodenitrogenation (HDN) catalysts exhibit promising activity in HDO of phenolic compounds such as phenol, anisole, and guaiacol.9-13 However, the metal-sulfide catalysts suffer from deactivation in the presence of high water content and the continuous addition of sulfur is required in the reactant stream to maintain the catalysts in the sulfide form. In addition, some supported noble metals such as Ru, Rh, Pd, Pt, and Re, as well as base metals, such as Cu, Ni, Fe and their heterometallic alloys are also active for hydrogenation / hydrogenolysis reactions, but the HDO process over these catalysts required high H₂ pressure, which also result in aromatic ring saturation.¹⁴⁻¹⁸ High pressure process would lead

to high operational cost.¹⁹ Therefore, it is necessary to develop a HDO process employing low cost catalysts with high stability and low H_2 pressure.

Recently, many studies on vapor phase HDO of ligninderived phenols via C-O bond cleavage without hydrogenating the aromatic ring under atmosphere H_2 were reported.^{6,20} Olcese and co-workers showed that Fe/SiO₂ could be used as catalyst in vapor phase HDO of guaiacol, while the yield of aromatic hydrocarbons was only 38%.^{21,22} Wang's group synthesized carbon-supported bimetallic Pd-Fe catalysts which have a good HDO activity of guaiacol and m-Cresol with good aromatic hydrocarbons yield.23-25 Nie and co-workers employed the bimetallic catalyst Ni-Fe/SiO₂ for catalytic conversion of m-cresol into toluene via deoxygenation reaction.²⁶ Metal phosphides, such as Ni₂P, also demonstrate high HDO activity for conversion of lignin-derived phenols. Wu and co-workers conducted atmospheric hydrodeoxygenation of guaiacol over nickel phosphide with different supports, finding that Ni₂P/SiO₂ prefers to produce aromatic hydrocarbons.²⁷ Besides the above catalysts, molybdenum-based catalysts, such as Mo₂C, Mo₂N and MoO₃, have shown good activity and selectivity on the vapor phase HDO of lignin-derived phenols. Ghampson and coworkers used Mo₂N and Mo₂N supported on activated carbon, Al₂O₃ and SBA to catalyze guaiacol HDO, observing a high activity and a significant conversion of guaiacol to phenol. They found that the active site for catalyzing guaiacol conversion are the Mo₂N and Mo oxynitride on the catalyst surface. Furthermore, their experiments also showed that the bimetallic nitride catalyst CoMoN gave higher yields of deoxygenated products than the monometallic nitride catalyst, but the overall activity of the monometallic nitride catalyst was higher than that of the bimetallic nitride.²⁸⁻³⁰ Lee and coworkers conducted selective vapor phase HDO of anisole to benzene over MoC₂, and the selectivity of benzene could reach about 90%.^{31,32} MoC₂ was also used to catalyze HDO of ligninderived phenolic compound mixtures containing *m*-cresol, anisole, 1,2-dimethoxybenzene, and guaiacol, and showed good catalytic activity at ambient pressure.33 However, the carbide catalyst showed fast deactivation by oxidation with water, which is a challenge for the catalyst system.³⁴ In addition, MoOx was employed to catalyze HDO of lignin-derived phenols under atmosphere H₂. Prasomsri and co-workers found that MoO₃ is active and selective for a direct C-O bond cleavage of guaiacol in a vapor phase over a packed-bed flow reactor, producing phenol and hydrocarbons with selectivity of 29.3% and 53.5%, respectively.³⁵⁻³⁸

N-doped carbon (NC), as a kind of fascinating material, has attracted worldwide attention recently.^{39,40} Because of the incorporation of nitrogen atoms in the carbon architecture can enhance chemical, electrical, and functional properties, it has been widely applied in flexible electronics, energy conversion/storage devices, and catalyst supports.⁴¹⁻⁴⁶ Xu and co-workers synthesized Pd nanoparticles supported on N-doped carbon and catalyzed bio-oil upgrading.⁴⁷ Li and co-workers synthesized Pd/N-doped carbon for catalytic hydrogenation of

phenol, and found N-doped carbon could strongly promote the chemoselective reduction of phenol.^{48,49}

In this study, a new molybdenum-based catalyst (MoOx@NC) for selective HDO of lignin-derived phenols was synthesized. MoOx@NC catalysts were synthesized via copyrolysis of biomass and (NH₄)₆Mo₇O₂₄•4H₂O in one step. The catalysts prepared at different pyrolysis temperature were obtained. Guaiacol was served as the model compound to test the catalytic activity. The factors which may affect the catalytic performance of MoOx@NC catalysts in the HDO process, including catalysts (C-600, NC-600, MoOx@C, and MoOx@NC-T), reaction temperature, WHSV, residence time and the content of guaiacol in mixture, were investigated systematically. Different lignin-derived phenols and dimmers were tested to produce aromatic hydrocarbons in this study. Furthermore, lifetime of MoOx@NC catalyst was measured. In addition, catalysts were characterized by elemental analysis, scanning electron microscope (SEM), Brunauer-Emmett-Teller surface area (BET), X ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

2. Experimental Section

2.1 Chemicals

Anisole (AR), benzaldehyde (AR), phenol (AR), m-cresol (AR), benzene (AR), toluene (AR), xylene (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. Eugenol (AR), and n-propylbenzene (AR) were purchased from Shanghai aladdin Biochemical Technology Co., Ltd. Guaiacol (AR), diphenyl ether (AR), 1,2-diphenylethane (AR), and mesitylene (AR) were purchased from Tokyo Chemical Industry Co. Ltd. (NH₄)₆Mo₇O₂₄•4H₂O was purchased from Alfa Aesar Co. Ltd. All these chemicals were used as received without any further purification. N₂ (99.999%), H₂ (99.999%), Ar (99.999%), NH₃ (\geq 99.5%), and He (99.999%) were purchased from Nanjing Special Gases Factory.

2.2 Catalyst preparation

For synthesis of MoOx@NC: The MoOx@NC catalysts were synthesized by direct pyrolysis of (NH₄)₆Mo₇O₂₄•4H₂O and microcrystalline cellulose under ammonia condition, which was conducted in a pyrolysis reactor. The tubular quartz pyrolysis reactor was placed in an electrical furnace with a PID temperature controller and the temperature of the experimental system was monitored by a K-type thermocouple. Before the pyrolysis process (Figure S1), 10.0 g of cellulose and a certain amount of (NH₄)₆Mo₇O₂₄•4H₂O solution were mixed in a flask and shaken at a constant temperature for 12 hours. Thereafter, water in the mixture was evaporated under reduced pressure. Finally, the solid residue was dried again at 110 °C to remove the moisture and the Mo-preloaded cellulose was obtained. Then, the Mo-preloaded cellulose was filled into the feed pipe. A 200 ml/min of NH₃ flowed through the pyrolysis system to remove air. Until the temperature reached the pre-set value, the mixture was fed into the tubular quartz pyrolysis reactor

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through a piston. The volatiles produced during pyrolysis were condensed by cold water to obtain bio-oil. After the fast pyrolysis process, the solid residue was kept in the reaction zone for another 2 hours for further carbonization. Then, the reactor was cooled under N_2 flow (200 ml/min) to room temperature. At last the MoOx@NC-T (T: pyrolysis temperature) catalyst was obtained and grinded by the glass mortar. For synthesis of NC-600: cellulose was pyrolysized in the presence of ammonia at 600 °C for 2 hours (NC-600). For synthesis of C-600: cellulose was pyrolysized in the presence argon at 600 °C for 2 hours (C-600). For synthesis of MoOx@C: The pyrolysis process was similar to that of MoOx@NC-T, except that the carrier gas was changed to argon during pyrolysis.

2.3 Catalyst test

As shown in Figure S2, a bench-top continuous flow reactor consisting of a quartz tube reactor heated by a furnace and a condensation tube bathed in liquid nitrogen was used for these experiments. The catalyst bed supported by quartz wool was built up in the heating zone of the reactor. A certain concentration of phenol solution was fed into the reactor with a peristaltic pump under a certain flow rate and purged with H₂. Volatile products were trapped in the condensation tube cooled with liquid N₂. The gas product was collected with a gas bag. The detailed method for analyzing the products and processing data are provided in the supplementary information.

The conversion of phenols, the yield of aromatic hydrocarbons, phenols, gases and the selectivity of different aromatic hydrocarbons, were calculated from Equation (1) to (5).



2.4 Catalyst Characterization

The elemental contents of the catalysts were measured by atomic absorption spectrum (ICP/AAS, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The N_2 adsorption/desorption isotherms of the catalysts were measured at -196 °C using the COULTER SA 3100 analyzer to do the Brunauer-Emmett-Teller surface area (BET) analyses. Scanning electron micrographs of the MoOx@NC were obtained using a scanning electron microscope (SEM, Sirion 200, FEI Electron Optics Company, USA). Transmission electron microscopy (TEM) investigations were performed on a JEM-2100F instrument (JEOL, Japan). Powder X-ray diffraction (XRD) analysis of the catalyst was carried out on a theta rotating anode X-ray diffractometer (TTR-III, Rigaku, Japan) by Cu K α radiation (30 kV/160 mA, $\lambda = 1.54056$ Å) with a scan rate (2 θ) of 0.05° s-1. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB250 instrument (Thermo-VG Scientific, UK). The intensity of the XPS peaks was recorded as counts per second (CPS) and deconvoluted into subcomponents using a Gaussian (80%)-Lorentzian (20%) curve-fitting program (XPSPEAK 4.1 software), with a Shirley type background.

Table 1. The effect of the catalyst preparation conditions on the guaicol HDO process ^a.

Tuble 1. The effect of the edu	ilyst propu	dtion conditions	on the gauleon HDC	process .			
Entry	1	2	3	4	5	6	7
Catalyst	C-600	NC-600	MoOx@C-600	MoOx@NC-600	MoOx@NC-500	MoOx@NC-550	MoOx@NC-650
Conversion (%)	36.5	53.4	97.5	100	100	100	100
Overall yield	32.9	47.1	95.2	95.1	92.7	89.2	92
Gases	-	-	8.8	9.3	8.0	9.7	14.5
Coke	3.7	4.2	11.9	10.3	11.7	10.9	11.4
Aromatic hydrocarbons	10.3	16.7	59.8	68.8	46.5	49.7	58.2
Phenols	18.9	26.2	14.7	6.7	26.5	18.9	7.9
			Aromatic h	ydrocarbons			
Benzene	8.4	13.0	45.9	46.1	35.2	35.6	37.1
Tolunene	1.9	3.7	13.6	19.8	10.0	12.4	18.6
Other alkylbenzenes	0	0	0.3	2.9	1.3	1.7	2.5
			Pho	enols			
Phenol	1.5	0.9	9.2	3.3	17.9	12.1	1.8
anisole	17.4	24.5	1.5	1.7	4.1	3.6	3.4
cresol	0	0.8	2.7	1.4	3.7	2.0	1.1
other alkylphenols	0	0	1.3	0.3	0.8	1.2	1.6
a: The catalytic test condition	s: solvent:	mesitylene, gua	iacol concentration=	=50%. T=400 °C. W	HSV _{mixture} =1 h ⁻¹ , res	idence time =2.2s.	$P_{H2}=1$ atm. each

time-on-stream is 1h. b: The yield in this study is carbon yield.

3. Results

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3.1 Effect of catalyst preparation condition



Figure 1. Effect of the catalyst preparation temperature on the detailed carbon yield of different aromatic hydrocarbons and phenols.

Herein, a simple and green method was developed to prepare Molybdenum oxide @ N-doped carbon (MoOx@NC) via in situ pyrolysis of molybdenum precursor preloaded cellulose. Table 1 shows the effect of catalyst preparation condition on the catalytic activity of MoOx@NC catalyst. Seven kinds of catalysts were prepared under different conditions. As shown in entry 1 and 2, we firstly tested the catalytic activity of carbon (C-600) and N-doped carbon (NC-600) on the vapor phase HDO of guaiacol, and found that both carbon and N-doped carbon could catalyze HDO of guaiacol to form aromatic hydrocarbons and selectively cleaved C-O bond to form phenols. When C-600 was served as catalyst, the conversion of guaiacol was 35.6%, and the carbon yield of aromatic hydrocarbons and phenols was 10.3% and 18.9%, respectively. When the N-doped carbon (NC-600) was served as catalyst, the conversion of guaiacol was 53.4%, and the carbon yield of aromatic hydrocarbons and phenols was 16.7% and 26.3%, which was much higher than that of C-600. Therefore, N-doped carbon (NC-600) showed better catalytic performance for vapor phase HDO of guaiacol. In addition, the molybdenum oxide C-600 (MoOx@C-600)supported on and NC-600 (MoOx@NC-600) catalysts were also tested. As shown in entry 3 and entry 4, MoOx@NC-600 showed better catalytic performance than MoOx@C-600 did. When MoOx@NC-600 served as the catalyst, the conversion of guaiacol was 100%, and the carbon yield of aromatic hydrocarbons and phenols was 68.8% and 6.7%, respectively. While, when MoOx@C-600 served as catalyst, the conversion of guaiacol was 97.5%, and the carbon yield of aromatic hydrocarbons and phenols was 59.8% and 14.7%, respectively. Compared with the catalytic performance of the catalysts prepared under N2 atmosphere, the catalyst prepared under ammonia atmosphere could produce more aromatic hydrocarbons and fewer phenols. Therefore, the

catalyst prepared under ammonia atmosphere could enhance the HDO performance.

Because MoOx@NC catalysts were prepared via an in situ pyrolysis process, the pyrolysis temperature was an important parameter to affect the catalyst performance. Entry 4 to entry 7 in Table 1 shows the guaiacol conversion and the detailed product distribution catalyzed by MoOx@NC catalysts prepared at different pyrolysis temperatures. Figure 1 shows the detailed carbon yield of different aromatic hydrocarbons and phenols. As shown in Table 1, under the selected conditions, all the guaiacol conversion was 100%. The carbon yield of coke didn't change significantly, and kept about 11%. The catalyst preparation temperature affected the carbon yield of aromatic hydrocarbons and phenols significantly. When the MoOx@NC-500 served as catalyst, the carbon yield of aromatic hydrocarbons and phenols was 46.5% and 26.5%, respectively. With the catalyst preparation temperature increasing to 600 °C, the carbon yield of aromatic hydrocarbons reached 68.8% and the carbon yield of phenols was only 6.7%. If the catalyst preparation temperature further increased to 650 °C, the carbon yield of aromatic hydrocarbons decreased, while the carbon yield of phenols increased. As shown in Figure 1, the carbon yield of phenol and m-cresol decreased with the catalyst preparation temperature increasing. When it was 600 °C, the highest carbon yield of benzene (46.1%) and toluene (19.8%) was obtained. Therefore, 600 °C was the suitable pyrolysis temperature for preparing the HDO catalyst, and MoOx@NC-600 was the suitable catalyst for catalytic vapor phase HDO of lignin-derived phenols.

3.2 Effect of reaction conditions on the vapor phase HDO of guaiacol

3.2.1 HDO reaction temperature

Based on the above study, we found that MoOx@NC-600 was the optimal catalyst for catalytic HDO of guaiacol under atmosphere H₂. However, the carbon yield of aromatic hydrocarbons was only about 68.8%, and there was still some phenols producing via partial HDO process. Herein, we further investigated the reaction conditions on the vapor phase HDO, which could also affect the product distribution and yield. Firstly, the effect HDO reaction temperature was investigated in the range of 300 °C and 600 °C over MoOx@NC-600 catalyst. Figure 2 shows the guaiacol conversion and the overall yield of coke, gases, aromatic hydrocarbons and phenols (a); the detailed carbon yield of different aromatic hydrocarbons and phenols (b) at different HDO reaction temperatures. The detailed product distributions at different temperatures are given in the supplementary information Table S3. As shown in Figure 2, the guaiacol conversion and the carbon yield of coke, gases, aromatic hydrocarbons and phenols were sensitive to the HDO temperature. With the temperature increasing from 300 to 600 °C, the carbon yield of gases increased from 4.2% to 16.2%. In contrast, the carbon yield of coke decreased from 19.5 to 4.8%. It could be caused by that higher temperature promoted phenols deep cracking to form non-condensable gas products

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Figure 2. Effect of HDO temperature on HDO of guaiacol in over MoOx@NC-600; (a) overall yield; and (b) detailed carbon yield of different aromatic hydrocarbons and phenols. (Reaction condition: Catalyst=MoOx@NC-600, solvent: mesitylene, guaiacol concentration =50%, WHSV_{mixture}=1 h⁻¹, residence time =3.3s, P_{H2}=1 atm.)

and prevented the coke formation. When the HDO reaction was below 400 °C, the guaiacol conversion could not reach 100%. Meanwhile, the main detected products in the liquid were not aromatic hydrocarbons but phenols, which were produced via partial HDO process. Phenol was the main product in phenols. When the HDO reaction temperature was at 350 °C, the carbon yield of phenols reached 63.9% (Figure 2a), and the carbon yield of phenol was 50.9% (Figure 2b). Lower reaction temperature prevented the catalyst activity, and lead to partial deoxygenation reaction. At 400 °C, with a full guaiacol conversion, the product distributions also changed dramatically. Aromatic hydrocarbons became the main products. The carbon yield of phenols decreased from 63.9% to 6.7%, while the carbon yield of aromatic hydrocarbons increased from 6.1% to 68.8%. Benzene and toluene were the main products in the aromatic hydrocarbons. The carbon yield of other alkylbenzenes (including xylenes) was very low. When the HDO reaction temperature increased to 450 °C, the carbon yield of aromatic hydrocarbons reached the maximum (70.2 %) and the carbon yield of benzene and toluene was 51.8% and 15.0%, respectively (Figure 2b). Conversely, the carbon yield of phenols reached the minimum (only 1.8%). If the reaction

Table 2. Effect of WHSV.							
Entry	1	2	3	4			
WHSV (h ⁻¹)	0.5	1.0	1.5	2.0			
Conversion (%)	100	100	100	96.3			
Overall yield	82.9	92.3	91.1	94.1			
Gases	13.8	13.4	12.5	10.7			
Coke	8.2	6.9	7.6	8.1			
Aromatic hydrocarbons	60.9	70.2	65.2	64.1			
Phenols	0	1.8	5.8	11.2			
Aromatic hydrocarbons							
Benzene	41.9	51.8	46.3	43.9			
Tolunene	14.8	15.0	15.2	16.3			
Other alkylbenzenes	4.2	3.4	3.7	3.9			
Phenols							
Phenol	0	0.7	1.1	4.3			
anisole	0	0.6	0.8	1.2			
cresol	0	0.5	2.9	5.0			
other alkylphenols	0	0	1.0	0.7			
The catalytic test condition: solvent: mesitylene, guaiacol concentration=50%, T= 450 °C, residence time =2.2 s; P_{H2} =1 atm, each time on stream is 1h c: The yield in this study is each on yield							

temperature further increased (500°C, and 600 °C), the carbon yield of aromatic hydrocarbons decreased, while the carbon yield of phenols increased. Higher reaction temperature may also cause the catalyst deactivation, and lead to the partial deoxygenation to form phenols, which could be the reason that the carbon yield of phenols increased with the reaction temperature further increasing. Thus, 450 °C was the optimal reaction temperature for HDO guaiacol over MoOx@NC-600 under atmosphere H₂.

3.2.2 WHSV

In addition to HDO reaction temperature, the effect of WHSV was also investigated in this study. Table 2 shows the detailed product distributions at different WHSV. The WHSV was defined as the ratio of the mass flow rate of guaiacol/mesitylene mixture to the mass of catalyst used in the reactor. During the experiments, the mass flow rate of guaiacol ranged from 0.5-2 g h^{-1} while the mass of catalyst was kept constant at 1 g. The HDO reaction temperature was kept at 450 °C. As shown in Table 2, all the guaiacol conversion was 100% in the range of 0.5 to 1.5 h⁻¹. When the WHSV increased to 2 h⁻¹, the conversion decreased to 96.3%. Meanwhile, the carbon yield of gas and coke decreased from 13.8% to 10.7% with the WHSV increasing from 0.5 to 2 h⁻¹. The carbon yield of coke kept about 7.5%. The carbon yield of aromatic hydrocarbons and phenols was affected by WHSV significantly. When the WHSV was at $0.5 h^{-1}$, no phenols were detected, and the carbon yield of aromatic hydrocarbons was about 60.9%. With the WHSV increased from 0.5 to 1 h⁻¹, the carbon yield of aromatic hydrocarbons and phenols increased from 60.9% and 0% to 70.2% and 1.8%, respectively. If the WHSV further increased to 1.5 h⁻¹ and 2 h⁻¹, the carbon yield of aromatic hydrocarbons

Entry	1	2	3	4				
catalyst usage (g)	0.5	1.0	1.5	2.0				
Residence time (s)	1.1	2.2	3.3	4.4				
Conversion (%)	100	100	100	100				
Overall yield	93.8	92.3	96.5	94.3				
Gases	10.7	13.4	12.7	13.2				
Coke	6.2	6.9	6.3	7.8				
Aromatic hydrocarbons	54.8	70.2	76.8	73.3				
Phenols	22.1	1.8	0.7	0				
Aromatic hydrocarbons								
Benzene	39.3	51.8	53.9	50.3				
Tolunene	13.8	15.0	18.1	16.6				
Other alkylbenzenes	1.7	3.4	4.8	6.4				
Phenols								
Phenol	11.2	0.7	0.5	0				
anisole	4.6	0.6	0.2	0				
cresol	5.3	0.5	0	0				
other alkylphenols	1.0	0	0	0				
The catalytic test	condition:	solvent:	mesitylene,	guaiacol				
concentration=50%, T= 450 °C, WHSV _{mixture} =1 h ⁻¹ , P _{H2} =1 atm, each								
time-on-stream is 1h. c: The yield in this study is carbon yield.								

started to decrease. Meanwhile, the carbon yield of phenols increased with the WHSV further increasing. Thus, the optimal WHSV was 1 h^{-1} for catalytic HDO of guaiacol over MoOx@NC-600 under atmosphere H₂.

3.2.3 Residence time

To further optimize the reaction conditions of catalytic HDO of guaiacol over MoOx@NC-600 under atmosphere H₂, the effect of residence time was also investigated via changing the catalyst usage from 0.5 g to 2g and fixing the reaction temperature, H₂ flow rate, and WHSV at 450 °C, 70 ml/min, and 1 h⁻¹. Herein, the residence time was in the range of 1.1s and 4.4s. Table 3 shows the detailed product distributions at different residence time. The guaiacol conversion, and the carbon yield of coke and gas were not affected by the residence time significantly. With the residence increasing from 1.1s to 4.4s, all the guaiacol conversion was 100%, and the carbon yield of coke and gas kept at about 7% and 13%, respectively. However, the carbon yield of aromatic hydrocarbons and phenols was very sensitive to the residence time. When the residence time was at 1.1s, the carbon yield of aromatic hydrocarbons and phenols was 54.8% and 22.1%, respectively. Then with the residence time increasing from 1.1s to 3.3 s, the carbon yield of aromatic hydrocarbons increased to 76.8%, while the carbon yield of phenols decreased 0.7%. If the residence time further increased to 4.4s, no phenols were detected. However, the carbon yield of aromatic hydrocarbons also decreased. Therefore, the optimal residence time was 3.3 s, and the catalyst usage was 1.5g. Meanwhile, the carbon yield of benzene and toluene reached 53.9% and 18.1%, respectively.

3.2.4 Guaiacol concentration

Besides the effect of reaction temperature, WHSV, and residence time, the effect of guaiacol concentration in mesitylene was investigated in the range of 20% to 100%. Table 4 shows the detailed product distributions of catalytic HDO of guaiacol with different concentration. As shown in Table 4, the guaiacol conversion and carbon vield of gas were not affected by guaiacol concentration significantly. The guaiacol conversion was kept at 100%, and the carbon yield of gases was about 12%. However, the carbon yield of coke, aromatic hydrocarbons and phenols was affected by the guaiacol concentration. With the guaiacol concentration increasing from 20% to 100%, the carbon yield of coke and phenols increased from 2.7% and 0% to 12.4% and 33.3%, respectively. Meanwhile, the carbon yield of aromatic hydrocarbons decreased from 83.3% to 39.8%. The lower guaiacol concentration, the less coke formation, and the more aromatic hydrocarbons production. Therefore, the optimal guaiacol concentration was 20%. Meantime, the carbon yield of benzene and toluene was 65.6% and 15.5%.

Through systematically investigating the parameters (such as: reaction temperature, WHSV, residence time, and concentration) in the vapor phase HDO of guaiacol under atmosphere H_2 , the optimal reaction conditions for vapor phase HDO of guaiacol was at 450 °C, 1 h⁻¹. The concentration of feed was 20%, and the residence time was about 3.3 s. The carbon yield of aromatic hydrocarbons was 83.3%, and no phenols was detected. The carbon yield of benzene, toluene and alkylbenzenes was 65.7%, 15.5%, and 2.1%, respectively.

3.3 Vapor phase HDO of different lignin-derived compounds over MoOx@NC catalyst

Based on the above study, guaiacol could be efficiently converted to aromatic hydrocarbons *via* vapor phase HDO process over MoOx@NC catalyst. In order to investigate the applicability of the catalyst, other six kinds of lignin-derived

Table 4. Effect of guaiacol concentration in mesitylene.

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Entry	1	2	3	4				
Concentration	20%	50%	80%	100%				
Conversion (%)	100	100	100	100				
Gases	11.6	12.7	11.0	11.8				
Coke	2.7	6.3	8.9	12.4				
Aromatic hydrocarbons	83.3	76.8	50.0	39.8				
Phenols	0	0.7	23.2	33.3				
Aromatic hydrocarbons								
Benzene	65.7	53.9	37.1	28.2				
Tolunene	15.5	18.1	9.9	8.1				
Other alkylbenzenes	2.1	4.8	3.0	3.5				
Phenols								
Phenol	0	0.5	17.3	23.4				
anisole	0	0.2	1.9	3.6				
cresol	0	0	3.8	6.0				
other alkylphenols	0	0	0.2	0.3				
The catalytic test condition: $T=450$ °C, residence time = 3.3 s. WHSV								

The catalytic test condition: T=450 °C, residence time =3.3 s, WHSV_{mixture} =1 h⁻¹, P_{H2} =1 atm, each time-on-stream is 1h. c: The yield in this study is carbon yield.

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	Vield	Aromatic hydrocarbons and yields ^b			
Feed	(C %)	Benzene	Toluene	Other alkylbenzenes	
ОН	90.6	90.6	N.D	N.D	
HO	87.3	10.3	77.0	N.D	
< →−o'	82.8	54.3	23.0	4.5	
✓ ^o	82.0	12.1	61.7	8.2	
	73.2	12.6	5.3	55.3	
	87.2	87.2	N.D	N.D	
	70.9	40.5	2.1	28.3	

Table 5. Vapor phase HDO of different lignin-derived phenols over MoOx@NC-600 under atmosphere H2.ª

a: All the feed conversion was 100%. The catalytic test conditions: guaiacol concentration=20%, T=450 °C, WHSV=1 h-1, residence time =3.3s, P_{H2}=1 atm, each time-on-stream is 1h. b: The yield in this study is carbon yield.

compounds including phenol, anisole, m-cresol, benzaldehyde, eugenol, diphenyl ether, and phenethoxybenzene were also catalyzed by MoOx@NC to produce aromatic hydrocarbons. For the simple lignin-derived compounds (phenol, m-cresol, anisole and benzaldehyde), MoOx@NC-600 showed good catalytic activity for vapor phase HDO to produce aromatic hydrocarbons. The carbon yield of aromatic hydrocarbons was above 80%. When benzaldehyde served as raw material, the carbon yield of the main product, toluene, was 61.7%. It indicated that MoOx@NC-600 can catalyze HDO of aldehyde group in addition to removal the methoxyl and phenolic hydroxyl groups. More interestingly, 1,2-diphenylethane could be detected in the products, and the carbon yield of 1,2diphenylethane was 8.2%. 1,2-Diphenylethane could be produced via a coupling reaction of benzaldehyde catalyzed by N-doped carbon, which had some basic sites. Eugenol could also be effectively converted to aromatic hydrocarbons by MoOx@NC-600 catalyst. Meanwhile, allyl group in eugenol was hydrogenated to propyl group. Thus, propyl benzene was the main HDO products from eugenol. MoOx@NC-600 could catalyze lignin dimer model compounds (diphenyl ether, phenethoxybenzene) HDO. When diphenyl ether served as the feed, benzene was the only aromatic hydrocarbons product, and the carbon yield of benzene reached 87.2%. When phenethoxybenzene served as the raw material, the carbon yield of benzene could reach 40.5% (theoretical carbon yield =42.8%), indicating MoOx@NC-600 can effectively remove the phenolic hydroxyl groups. However, the carbon yield of ethylenzene was only 28.3%, which means MoOx@NC-600 cannot effectively remove the alcohol hydroxyl group.

3.4 Catalyst stability



Figure 3. The catalyst stability; (a) conversion and overall yield; The catalyst stability is very important in the vapor phase HDO

(b) detailed carbon yield of different aromatic hydrocarbons and phenols. (Reaction condition: solvent: mesitylene, guaiacol T=450 °C, residence time =3.3sconcentration=20%, WHSV_{mixture}=1 h⁻¹)

process. Prasomsri et al. reported that molybdenum oxides showed a fast deactivation in the vapor phase HDO of cresol.³² When the HDO reaction temperature was at 400 °C, the cresol conversion decreased from 100% to 10% after a 4 hours' reaction. Herein, the stability of MoOx@NC was also investigated at 450 °C using guaiacol as the feed. Figure 3 shows the guaiacol conversion and carbon yield of aromatic hydrocarbons and phenols (a); the detailed carbon yield of different aromatic hydrocarbons and phenols (b) at different time on streams. The detailed product distributions are given in Table S4 in the supplementary information. As shown in Figure 3a, in the early 7.5 hours, the guaiacol conversion kept 100%, and the carbon yield of aromatic hydrocarbons and phenols kept above 80% and 5%. Meanwhile, the carbon yield of benzene, toluene was about 60% and 20% (Figure 3b), respectively. Anisole was the main component in the phenols. With the reaction time further extending to 20 hours, the guaiacol conversion still kept 100%. However, the carbon yield

of aromatic hydrocarbons kept decreasing. Meanwhile, the changing trend of benzene and toluene was constant with that of aromatic hydrocarbons. Conversely, the carbon yield of phenols increased. When the reaction time reached 20 hours, the carbon yield of aromatic hydrocarbons decreased to 42.7%, meanwhile, the carbon yield of phenols increased to 25.8%. To investigate the reason for the selectivity of aromatics drops substantially after 7.5 hours and the change of catalyst structure, the catalyst after the reaction was characterized by elemental analysis, N2 adsorption/desorption and XPS. Table S5 shows the physicochemical properties of MoOx@NC-600 before and after reaction. The elemental contents, surface elemental contents, BET surface area and pore volume of the catalyst changed a lot after reaction. The content of carbon on the surface increased. The content of Mo, N, and BET surface area and pore volume decreased a lot. It indicated that coke formed after the reaction, and the coke may cover the active site of the catalyst, which caused the catalytic activity of the MoOx@NC-600 decreased.

3.5 Catalyst characterization

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According to the above study, we found that MoOx@NC-600 was the optimal catalyst for catalytic vapor phase HDO of lignin-derived phenols under atmosphere H₂. Table 6 shows the physicochemical properties of MoOx@NC-600 catalyst, including BET surface area, elemental contents, and catalyst surface elemental contents. The BET surface area of MoOx@NC-600 was 81.0 m²/g (The adsorption / desorption of MoOx@NC-600 was shown in Figure S3 in the supplementary information). The content of C, H, N, and O was 47.2%, 1.7%, 4.5% and 20.5%, respectively. The metal loading of MoOx@NC-600 was about 26.1%. For comparison, the catalyst surface contents were also measured by XPS. The content of C, N, O, Mo was 85.7%, 6.1%, 6.5%, and 1.7%, respectively. The content of carbon and nitrogen on the catalyst surface was much more than that of the bulk catalyst. In contrast, the content of Mo and oxygen on surface was lower than that of the bulk catalyst. It indicated that N-doped carbon might form on the surface of MoOx particles, which could be beneficial for the catalyst stability.

XRD was used to monitor the crystallite phase composition of MoO₂, NC-600, and MoOx/NC-600. As shown in Figure 4, amorphous carbon in the NC-600. The characteristic diffraction peaks of MoO₂ patterns were at 20 of 26.1°, 36.9°, 41.6°, 53.3°, 60.4°, 66.7°, and 78.8°. The diffraction peaks at 20 of 26.1°, 36.9°, 41.6°, 53.3°, 60.4°, 66.7°, and 78.8° were also existed in the XRD patterns of MoOx@NC-600, indicating that the MoOx in the MoOx@NC-600 was MoO₂.



Figure 4. XRD patterns of NC-600 and MoOx@NC-600.



Figure 5. XPS curves of MoOx@NC-600; (a) Survey XPS curves of O 1s, N 1s, C 1s and Mo 3d of the catalyst. (b) X-ray photoelectron Mo 3d spectra of Mo 3d of MoOx@NC-600 catalyst. (c) X-ray photoelectron N 1s spectra of MoOx@NC-600 catalyst. (d) X-ray photoelectron O 1s spectra of MoOx@NC-600.

In order to further evaluate the electronic state of molybdenum, nitrogen and oxygen presenting in the catalyst, the binding energies of the relative substances were determined by XPS. Although the diffraction peaks shown in XRD patterns

Table 6. Physicochemical p	roperties of MoOx@NC-600.
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BET surface area m ² /g	Elemental contents (wt %)	С	Н	N	Мо	0
81.0	Catalyst elemental contents ^a	47.2	1.7	4.5	26.1	20.5
	Catalyst surface elemental contents ^b	85.7	-	6.1	1.7	6.5

a: The content of C, H, and N was determined by elemental analyzer. The content of molybdenum in MoOx@NC-600 was measured by atomic absorption spectrum (Escalab 250Xi, Thermo Fisher). b: The elemental content of the catalyst surface was determined by XPS.

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can only attribute to MoO₂, from Mo 3d in Figure 5b, the Mo 3d doublet contained mixed chemical states with contributions from Mo^{δ^+}, Mo^{4^+}, Mo^{5^+}, and Mo^{6^+}. In details, the 3d5/2 energy at 229.0 eV, corresponding to Mo with an oxidation state between +4 and +2, is assigned to Mo₂N species.²⁸⁻³⁰ Mo₂N is an effective catalyst for catalytic HDO of lignin-derived phenols.^{28,30} The 3d5/2 energy at 229.7 eV, corresponding to Mo^{4+} , can be assigned to MoO_2 . ^{35,36} The 3d5/2 energy at 230.8 eV peak could be assigned to molybdenum oxynitrides.^{30, 50-52} The molybdenum oxynitrides is similar to MoOxCyHz, which is associated with the active sites and the HDO activities.^{35,36} The percentage of Mo^{6+} , Mo^{5+} , Mo^{4+} and Mo^{6+} was 42.9 : 12.5 : 34.9: 9.7. In addition, no signal corresponding to Mo metal (i.e., Mo⁰ state) was detected. From N1s in Figure 5c, the catalyst displayed 4 binding energies peaks at 395.0 eV, 396.6 eV, 398.5 eV and 400.9 eV. The peak at 395.0 eV could be attributed to the molybdenum oxynitrides; the peak at 396.6 could be attributed to the Mo-N in the Mo₂N; the peak at 398.5 eV could be attributed to pyridinic-like $(398.5 \pm 0.2 \text{ eV})$

nitrogen atoms incorporated into graphitic sheets (pyridinic-N); the peak at 400.7 eV can be mainly assigned to pyrrolic/ pyridone-N.⁵³⁻⁵⁵ From O 1s in Figure 5d, three peaks at 530.5 eV, 532.0 eV and 533.2 eV could be attributed to the Mo-O, OH- and H₂O, respectively.^{56,57}

Figure 6 shows the SEM, TEM, and EDS mapping of MoOx@NC-600. Figure 6a showed porous morphology on rough carbon sheet, which is similar to the typical pyrolytic biochar reported by Liu and co-workers.^{57,58} TEM images and the corresponding elemental mapping analysis of MoOx@NC-600 (Figure 6b-f) could further reveal the morphology of the MoOx@NC-600 catalyst. Figure 6b showed that the MoOx particle was irregular, and the particle size of MoOx reached about 200 nm. The EDS mapping (Figure 6d-f) shows the MoOx had been successfully embedded on the N-doped carbon. In addition, it also indicated that N-doped carbon was deposed on the surface of MoOx particle, which would be beneficial for the catalyst stability.



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Figure 6. The SEM, TEM and EDS mapping of MoOx@NC-600; a) SEM analysis; b) TEM analysis; c) Elemental mapping of Mo; d) elemental mapping of C; e) elemental of O; f) elemental of N.

4. Discussion

In the above study, we found that the pyrolysis temperature was important to the catalytic activity of MoOx@NC catalysts. To further illustrate the effect of pyrolysis temperature on the catalytic activity of MoOx@NC catalysts, these catalysts were also characterized by elemental analysis (Table S1) XRD (Figure 7), and XPS (Figure 8). As shown in Table S1, with the pyrolysis temperature increasing, the content of molybdenum increased, while the content of carbon and nitrogen decreased. However, when the pyrolysis temperature was 600 °C, the content of nitrogen strated to increase, which could be due to the molybdenum nitride formation in the pyrolysis process

(Shown in Figure S1). XRD patterns (Figure 7) showed that molybdenum existed mainly as MoO_2 when the pyrolysis temperature ≤ 600 °C. When the pyrolysis temperature increased to 650 °C, the diffraction peaks at 20 of 41.6°, 53.3°, 60.4° , 66.7° , and 78.8° disappeared. While, new diffraction peak at 20 of 43.3°, 53.5°, 62.8°, and 75.5° appeared. The new diffraction peak could be attributed to Mo_2N .

Furthermore, XPS curves (Figure 8) also showed that Mo 3d doublet contained mixed chemical states attributed to Mo^{δ^+} . Mo⁴⁺, Mo⁵⁺, and Mo⁶⁺. According to the previous studies, Mo⁵⁺ (corresponding to molybdenum oxynitrides), and Mo^{δ^+} (corresponding to Mo₂N) are active for catalytic HDO of lignin-derived phenols, while Mo⁶⁺ is not.²⁸⁻³⁰ In present system, with the pyrolysis temperature increasing, the percentage of Mo^{6+} kept about 44%, while the percentage of Mo^{5+} Mo^{4+} molybdenum (corresponding to oxynitrides), (corresponding to MoO₂), and Mo^{δ^+} (corresponding to Mo₂N) changed significantly. When the pyrolysis temperature was at 500 °C, the Mo 3d attributed to Mo^{4+} , Mo^{5+} , and Mo^{6+} . The signal (Mo^{δ^+}) corresponding to Mo₂N was not detected. The percentage of Mo⁶⁺, Mo⁵⁺, and Mo⁴⁺ was 43.4, 37.3 and 19.3, respectively. When the pyrolysis temperature increased to 550 °C, Mo^{δ^+} assigned to Mo_2N was detected and the percentage of Mo^{δ^+} was 5%. Then, the percentage of Mo^{δ^+} increased with the temperature further increasing. When the pyrolysis temperature was at 650 °C, the percentage of Mo^{δ^+} was 26.5%. By contrast, the percentage of Mo⁵⁺ decreased with the pyrolysis temperature increasing. When the pyrolysis temperature was at 650 °C, the percentage of Mo⁵⁺ was 12.3 %. For the Mo⁴⁺, when the pyrolysis temperature was ≤ 600 °C, the percentage of Mo4+ increased from 19.3% to 34.9%. If the pyrolysis temperature further increased to 650 °C, the percentage of Mo⁴⁺ decreased to 15.3%. When the pyrolysis temperature was at 600 °C, the percentage of Mo⁴⁺ was highest, and the catalyst also showed the best catalytic performance. In addition, the variation tendency of Mo⁴⁺ was consistent with the variation tendency of the catalyst catalytic performance. Therefore, besides the Mo^{5+} and $Mo^{\delta+}$, the Mo^{4+} should also be the active site in the MoOx@NC catalyst for catalytic HDO.



Figure 7. XRD patterns of MoOx@NC-T catalysts.

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B.E.(eV) Figure 8. XPS curves of Mo in different MoOx@NC-T catalysts. a): MoOx@NC-500; b) MoOx@NC-550; c): MoOx@NC-600; d) MoOx@NC-650.

5. Conclusion

In this study, a simple, and green method was developed to prepare Molybdenum oxide @ N-doped carbon (MoOx@NC) via in situ pyrolysis of molybdenum preloaded cellulose. MoOx@NC demonstrated excellent catalytic performance and stability on vapor phase HDO of lignin-derived phenols. Through the study of catalyst preparation condition, we found that N-doped carbon could catalyze HDO of guaiacol to form aromatic hydrocarbons and selectively cleaved C-O bond to form phenols. When the pyrolysis temperature was at 600 °C, the catalysts (MoOx@NC-600) exhibited the best catalytic performance on vapor phase HDO of guaiacol. Through systematically investigating the parameters (such as: reaction temperature, WHSV, residence time, and concentration) in the vapor phase HDO of guaiacol under atmosphere H₂, the optimal reaction conditions for vapor phase HDO of guaiacol was at 450 °C, 1 h⁻¹. The concentration of guaiacol in mesitylene was 20%, and the residence time was about 3.3 s. The carbon yield of aromatic hydrocarbons was 83.3%, and no phenols was detected. The carbon yield of benzene, toluene and alkylbenzenes was 65.7%, 15.5%, and 2.1%, respectively. Other lignin-derived phenols were also investigated and achieved good results by using MoOx@NC-600. Furthermore, the catalysts were also characterized by elemental analysis, AAS, BET, XRD, XPS, TEM, and EDS mapping. Mo⁴⁺ could be the main active site of the MoOx@NC catalysts, and the Ndoped carbon formed on the surface of MoOx particles could also be beneficial for the catalyst stability. Therefore, the high catalytic performance of MoOx@NC-600 toward ligninderived phenols HDO can be attributed to the synergistic effect of carbon supports and Mo^{5+} (molybdenum oxynitides), Mo^{5+} (Mo₂N) and Mo⁴⁺ on the surface of MoOx particles.

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Notes and references

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[†] Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [Pyrolysis reactor for preparing MoOx@NC catalysts and catalyst test; N₂ adsorption–desorption isotherms of MoOx@NC-600 catalyst; Physicochemical properties of catalysts, detailed product distributions of guaiacol HDO under different catalyst, reaction temperatures, reaction time]. See DOI: 10.1039/b000000x/

References

- 1. G. W. Huber, S. Iborra, A. Corma, Chem. Rev., 2006, 106, 4044-4098.
- 2. J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552.
- 3. A. V. Bridgwater, G. V. C Peacocke, *Renew. Sustain. Energ. Rev.*, 2000, 4, 1-73.
- 4. C. Liu, H. Wang, A. M. Karim, J. Sun, Y. Wang, *Chem. Soc. Rev.*, 2014, **43**, 7594-7623.

5. C. Li, X. Zhao, A. Wang, G. W. Huber, T. Zhang, *Chem. Rev.*, 2015, **115**, 11559–11624.

- 6. M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B. C. Gates, M. R. Rahimpour, *Energ. Environ. Sci.*, 2014, **7**, 103-129.
- 7. M. S. Talmadge, R. M. Baldwin, M. J. Biddy, R. L. McCormick, G.
- T. Beckham, G. A. Ferguson, S. Czernik, K. A. Magrini-Bair, T. D. Foust, P. D. Metelski, C. Hetrick, M. R. Nimlos, *Green Chem.*, 2014, **16**, 407-453.
- 8. D. E. Resasco, J. Phys. Chem. Lett., 2011, 2, 2294-2295.

9. J. B. Bredenberg, M. Huuska, J. Räty, M. Korpio, J. Catal., 1982, 77, 242–247.

- 10. A. Centeno, E. Laurent, B. Delmon, J. Catal., 1995, 154, 288-298.
- 11. E. Laurent, B. Delmon, Appl. Catal. A-Gen., 1994, 109, 77-96.
- 12. M. Ferrari, S. Bosmans, R. Maggi, B. Delmon, P. Grange, *Catal. Today*, 2001, **65**, 257–264.
- 13. V. N. Bui, D. Laurenti, P. Afanasiev, C. Geantet, *Appl. Catal. B-Environ.*, 2011, **101**, 239–245.
- 14. C. R. Lee, J. S. Yoon, Y.-W. Suh, J. W. Choi, J. M. Ha, D. J. Suh, Y. K. Park, *Catal. Commun.*, 2012, **17**, 54–58.

- 15. M. V. Bykova, D. Y. Ermakov, V. V. Kaichev, O. A. ulavchenko, A. A. Saraev, M. Y. Lebedev and V. A. Yafkovlev, *Appl. Catal., B-Environ.*, 2012, **113–114**, 296–307
- 16. Y. B. Huang, L. Yan, M. Y. Chen, Q. X. Guo, Y. Fu, *Green Chem.*, 2015, **17**, 3010-3017.
- 17. M. Y. Chen, Y. B. Huang, H. Pang, X. X. Liu, Y. Fu, *Green Chem.*, 2015, **17**, 1710-1717.

18. M. Asadieraghi, W. M. A. W. Daud, H. F. Abbas, *RSC Adv.*, 2015, 5, 22234-22255.

19. H. Wang, J. Male, Y. Wang, ACS Catal., 2013, 3, 1047-1070.

J. Sun, A. Karim, H. Zhang, L. Kovarik, X. Shari Li, A. J. Hensley, J.
 S. McEwen, Y. Wang, *J. Catal.*, 2013, **306**, 47–57.

- 21. A. J. R. Hensley, Y. Hong, R. Zhang, H. Zhang, J. Sun, Y. Wang. J. S. Mc Ewen, *ACS Catal.*, 2014, **4**, 3381–3392.
- 22. Y. C. Hong, H. Zhang, J. Sun, A. M. Karim, A. J. R. Hensley, M. Gu, M. H. Engelhard, J. S. McEwen, Y. Wang, *ACS Catal.*, 2014, **4**, 3335–3345.
- 23. R. Olcese, M. M. Bettahar, D. Petitjean, B. Malaman, F. Giovanella, A. Dufour, *Appl. Catal. B Environ.*, 2012, **115-116**, 63-73.
- 24. R. Olcesea, M. M. Bettaharb, B. Malamanc, J. Ghanbajac, L. Tibavizcoa, D. Petitjeana, A. Dufoura, *Appl. Catal. B Environ.*, 2013, **129**, 528-538.

25. L. Nie, P. M. de Souza, F. B. Noronha, W. An, T. Sooknoi, D. E., Resasco, J. Mol. Catal. A- Chem. 2014, **388**, 47-55.

- 26. S. K. Wu, P. C. Lai, Y. C. Lin, Catal. Let. 2014, 144, 878-889.
- W. S. Lee, Z. Wang, R. J. Wu, A. Bhan, J. Catal., 2014, 319, 44-53.
 I. T. Ghampson, C. Sepulveda, R. Garcia, B. G. Frederick, M. C.
- Wheeler, N. Escalona, W. J. DeSisto, *Appli. Catal. A-Gen.* 2012, **413-414**, 78-84.

29. I. T. Ghampson, C. Sepulveda, R. Garcia, L. R. Radovic, J. L. G. Fierro, W. J. DeSisto, N. Escalona, *Appl. Catal. A- Gen.* 2012, **439-440**, 111-124.

- 30. I. T. Ghampson, C. Sepulveda, R. Garcia, J. L. G. Fierro, N. Escalona, W. J. DeSisto, *Appl. Catal. A- Gen.* 2012, **435-436**, 51-60.
- 31. W. S. Lee, A. Kumar, Z. Wang, A. Bhan, ACS Catal., 2015, 5, 4104-4114.
- 32. C. J. Chen, W. S. Lee, A. Bhan, *Appl. Catal., A-Gen.*, 2016, **510**, 42-48.
- 33. E. Santillan-Jimenez, M. Perdu, R. Pace, T. Morgan, M. Crocker, *Catal.* 2015, **5**, 424-441.

34. T. Prasomsri, T. Nimmanwudipong, Y. Román-Leshkov, *Energy Environ. Sci.*, 2013, **6**, 1732-1738

35. T. Prasomsri, M. Shetty, K. Murugappan, Y. Román-Leshkov, *Energy Environ. Sci.*, 2014, **7**, 2660-2669.

36. T. Prasomsri, A. T. To, S. Crossley, W. E. Alvarez, D. E. Resasco, *Appl. Catal., B* 2011, **106**, 204-211.

- 37. X. Zhao, J. B. Zhua, L. Liang, C. Y. Li, C. P. Liu, J. H. Liao, W. Xing, *Appl. Catal. B-Environ.*, 2014, **154-155**, 177-182.
- K. Murugappan, C. Mukarakate, S. Budhi, M. Shetty, M. R. Nimlos, Y. Román-Leshkov, *Green Chem.*, 2016, DOI: 10.1039/C6GC01189F.
- 39. Y.Zhao, R. Nakamura, K. Kamiya, S. Nakanishi, K. Hashimoto, K. *Nature Commun.*, 2013.
- 40. J. Hou, C. Cao, F. Idrees, X. Ma, ACS Nano, 2015,9, 2556-2564.
- 41. Y. T. Gong, M. M. Li, H. R. Li, Y. Wang, Green Chem., 2015,17, 715-736.

43. C. M. A. Parlett, K. Wilson and A. F. Lee, *Chem. Soc. Rev.*, 2013, **42**, 3876–3893

44. P. Zhang, J. Yuan, T.-P. Fellinger, M. Antonietti, H. Li and Y. Wang, *Angew. Chem.*, *Int. Ed.*, 2013, **52**, 6028–6032.

45. D. C. Guo, J. Mi, G. P. Hao, W. Dong, G. Xiong, W. C. Li A. H. Lu, *Energ. Environ. Sci.*, 2013, **6**, 652–659.

46. X. Xu, Y. Li, Y. T. Gong, P. F. Zhang, H. R. Li, Y. Wang, J. Am. Chem. Soc., 2012, 134, 16987–16990.

47. X. Xu, H. R Li, Y. Wang, ChemCatChem. 2014, 6, 3328-3332

48. Y. Li, X. Xu, P. F. Zhang, Y. T. Gong, H. R. Li, Y. Wang, *RSC Adv.*, 2013, 3, 10973-10982.

49. W. J. Liu, K. Tian and H. Jiang, Green Chem., 2015, 17, 821-826.

50. T. Becue, J. M. Manoli, C. Potvin, G. Djega-Mariadassou, J. Phys. Chem. B, 1997, 101, 6429-6435.

51. P. Perez-Romo, C. Potvin, J. M. Manoli, M. M. Chehimi, G. Djega-Mariadassou, J. Catal., 2002, 208, 187-196.

- 52. S. W. Yang, C. Li, J. Xu, Q. In, *J. Phys. Chem. B*, 1998, **102**, 6986-6993.
- 53. K. Hada, M. Nagai, S. Omi, *J. Phys. Chem. B*, 2001, 105, 4084-4093.
 54. W. Kim, J. B. Joo, N. Kim, S. Oh, P. Kim, J. Yi, *Carbon*, 2009, 47, 1407-1411.

55. W. Luo, B. Wang, C. G. Heron, M. J. Allen, J. Morre, C. S. Maier, W. F. Stickle, X. Ji, *Nano Lett.*, 2014, **14**, 2225–2229.

56. Y. Q. Zhao, M. Lu, P. Y. Tao, Y. J. Zhang, X. T. Gong, Z. Yang, et *J. Power Sour.*, 2016, **307**, 391-400.

57. L. J. Xu, Q. Yao, J. Deng, Z. Han, Y. Zhang, Y. Fu, G. W. Huber, Q. X. Guo, *ACS Sustain. Chem. Eng.*, 2015, **3**, 2890-2899.

58. W. J. Liu, F. X. Zeng, H. Jiang and H. Q. Yu, *Bioresour*. *Technol.*, 2011, **102**, 3471-3479.

59. W. J. Liu, H. Jiang, K. Tian, Y. W. Ding and H. Q. Yu, *Environ. Sci. Technol.*, 2013, **47**, 9397-9403.

Graphic abstract



In situ synthesis of molybdenum oxide @ N-doped Carbon from biomass for selective vapor phase hydrodeoxygenation of lignin-derived phenols under atmosphere H₂

Lujiang Xu, Zheng Han, Ying Zhang, Yao Fu