

# CHEMISTRY & SUSTAINABILITY

# CHEMSUSCHEM

**ENERGY & MATERIALS** 

# **Accepted Article**

Title: Task-Specific Catalyst Development for Lignin-First Biorefinery toward Hemicellulose Retention or Feedstock Extension

Authors: Shi Qiu, Xuan Guo, Yong Huang, Yunming Fang, and Tianwei Tan

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201802130

Link to VoR: http://dx.doi.org/10.1002/cssc.201802130



WILEY-VCH

www.chemsuschem.org

## WILEY-VCH

# Task-Specific Catalyst Development for Lignin-First Biorefinery toward Hemicellulose Retention or Feedstock Extension

Shi Qiu, Xuan Guo, Yong Huang, Yunming Fang\*<sup>[a]</sup> and Tianwei Tan

Abstract: A novel catalytic reductive fractionation method for lignocellulosic biomass, termed as lignin-first biorefinery, is emerged with an emphasis on preferential depolymerization of the protolignin. However, in most studies, the lignin-first biorefinery is only effective for hardwood that contains a high S/G ratio of lignin building block, and the degradation of hemicellulose also takes place simultaneously to a certain degree. In this study, two task-specific catalysts were developed to realize hemicellulose retention or feedstock extension through the development of objectiveperformance-structure relationship. It is found that MoxC/CNT is highly selective in cleavage of bonds between carbohydrates and lignin and ether bonds in lignin during the catalytic reductive fractionation of hardwood, leading to a carbohydrate (both cellulose and hemicellulose) retention degree in solid product close to theoretical maximum and a delignification degree as high as 98.1%. Ru/CMK-3 is demonstrated to be effective in the catalytic reductive fractionation of softwood and grass, resulting from its weak acidity and high mesoporosity.

### 1. Introduction

Lignocellulosic biomass is a bio-macromolecule of cellulose, hemicellulose, and lignin polymers, bound by different linkages.<sup>[1]</sup> The purpose on effective utilization of both energy and chemical elements of biomass as biofuels, biomaterials, and bioenergy leads to extensive researches on biorefinery in the past decades.<sup>[2]</sup>

The first step in a typical biorefinery is to liberate sugars from biomass by pretreatment and subsequently enzymatic/chemocatalytic hydrolysis.<sup>[3]</sup> Until now, numerous pretreatment methods, such as steam explosion, acid, alkali, organosolv, ammonia, and ionic liquid pretreatments, have been developed.<sup>[4]</sup> However, most of these pretreatment methods leading to the structural change of lignin and the change is highly dependent on the pretreatment method and condition.<sup>[5]</sup> The decrease in ether bonds (e.g.,  $\beta$ -O-4 bond) of lignin and subsequent formation of new C-C linkages generally take place, which result in difficulties in depolymerization and utilization of the resulting lignin.<sup>[6]</sup>

Recently, together with the reconsideration of which part in biomass is better for biofuel production, a novel catalytic reductive fractionation method (also called as lignin-first

[a] S. Qiu, X. Guo, Dr. Y. Huang, Prof. Y. Fang, Prof. T. Tan National Energy R&D Research Center for Biorefinery Department of Chemical Engineering Beijing University of Chemical Technology 15 Beisanhuan East Road, Beijing, People's Republic of China E-mail: fangym@mail.buct.edu.cn biorefinery) for lignocellulosic biomass with an emphasis on preferential depolymerization of the protolignin, has been reported from several groups. Ferrini et al.<sup>[7]</sup> reported a Raney Ni and isopropanol/water solvent catalytic system with isopropanol as hydrogen donor. High degrees of delignification and cellulose retention in the pulp as well as the enzymatic processing of the pulp were demonstrated. Parsell et al.<sup>[8]</sup> presented a selective hydrogenolysis of protolignin with Zn modified Pd nanoparticles on carbon with external H<sub>2</sub>, focusing on the lignin monomers/oligomer production and the enzymatic conversion of the retained pulp. Bosch et al.<sup>[9]</sup> also reported a reductive fractionation of biomass into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. Up to date, the development of novel catalysts, understanding the reaction mechanism, and process optimization has been reported exclusively in this area. Very recently, Cao et al. reported that high energy density fuel could be produced from the oil obtained by lignin-first biorefinery with the help of catalyst optimization. [10]

Despite the preliminary promising results in reductive fractionation of lignocellulosic biomass, there are still several points need further study. Firstly, the amorphous hemicellulose is also degraded to some degree due to its fragile nature compared with crystalline cellulose in a typical lignin-first biorefinery. In a recent study, hemicellulose was found to undergo deacetylation over Raney Ni catalyst in isopropanol, and releasing acetic acid into the liquor.<sup>[10h]</sup> It would be an interesting option for the preservation of hemicellulose in the solid product together with cellulose and co-utilization in following bio-chemical conversions (e.g. ABE fermentation). Another important issue in the lignin-first biorefinery is the feedstock extension. In most of the above mentioned studies, designated feedstock (usually hardwood) is employed to demonstrate the potential of lignin-first concept. The reason behind is the high S/G ratio of lignin unit and consequently high β-O-4 linkages in hardwood.<sup>[11]</sup> However, in biomass, softwood has higher lignin content (between 25-35%) than that of hardwood (< 25 %).<sup>[12]</sup> Furthermore, the G type rich lignin in softwood has less oxygen and is better as a precursor for biofuel production.<sup>[13]</sup> Hence to make the lignin-first concept more applicable, it is important to extend the feedstock from hardwood to softwood and other G type lignin rich biomass.

The catalyst plays a very important role in above process. Sels, Beckman and other researchers provide different mechanistic insights on how catalysts can improve this process. <sup>[14]</sup> Hence we are interested to develop task specific catalysts for hemicellulose retention or feedstock extension purpose. For hemicellulose retention, it is important to improve the catalyst selectivity, that is, selective cleavage the linkages between carbohydrates and lignin and the ether bonds in lignin, and prevent the depolymerization of hemicellulose over catalyst. Molybdenum carbide/oxycarbide has been reported as a robust catalyst comparable to noble metals in biomass/lignin conversion, including hydrodeoxygenation of lignin model

Supporting information for this article is given via a link at the end of the document.



compounds (e.g., guaiacol, anisole, etc.) and lignin hydrogenolysis.<sup>[15]</sup> In some cases, Mo-based catalyst shows unique selectivity toward ether bond cleavage in lignin depolymerization.<sup>[16]</sup> It is thus interesting to test the possibility of Mo-based catalyst for hemicellulose retention. With respect to feedstock extension, the most important fundamental question is the different reactivities of the fragments from solvation of different types of lignin under reaction conditions.<sup>[17]</sup> It is generally believed that the lignin in softwood has a higher condensation degree and more C-C bond in nature,<sup>[18]</sup> hence it is important to understand the reactivities of these C-C rich fragments and develop catalyst accordingly.

Based on above discussion, task-specific (hemicellulose retention or feedstock extension) catalysts were developed for improving the lignin-first biorefinery. The fundamental understanding, structure-performance relationship of the developed catalysts as well as catalytic performance were discussed according to hemicellulose retention or feedstock extension, respectively.

#### 2. Results and Discussion

# 2.1 Hemicellulose retention in the lignin-first biorefinery of hardwood.

According to the discussion in the introduction section, the molybdenum carbide/oxycarbide catalysts were synthesized and tested in the catalytic reductive fractionation of hard wood.



Figure 1. XRD patterns of 10% Mo<sub>x</sub>C/CNT (a) prepared at different carbothermal reduction temperatures under H<sub>2</sub> and Mo (3d) XPS spectra deconvolution of fresh 10% Mo<sub>x</sub>C/CNT prepared at (b) 600 °C, (c) 700 °C, and (d) 800 °C.

#### 2.1.1 Controllable synthesis of Mo<sub>x</sub>C/CNT catalysts.

Mo<sub>x</sub>C/CNT catalysts were prepared by the deposition of ammonium heptamolybdate tetrahydrate (AHM) on CNT support

Samples	S <sub>BET</sub> (m²⋅g⁻¹)	Pore volume (cm <sup>3</sup> ·g <sup>-1</sup> )	Pore size (nm)	Carbon loss (wt%)	Mo loading (wt%)
Mo <sub>x</sub> C/CNTs 600	251.27	1.30	18.52	14	11.6
Mo <sub>x</sub> C/CNTs 700	183.48	0.81	16.20	50	20.0
Mo <sub>x</sub> C/CNTs 800	161.16	0.68	15.63	70	33.3

and a subsequent thermal treatment with hydrogen according to reported methods.<sup>[19]</sup> Different temperatures being 600, 700, and 800 °C were used to tailor the catalyst properties. The XRD patterns of the prepared catalysts are shown in Figure 1a. The AHM/CNT sample, without further carbothermal hydrogen reduction treatment, shows a diffraction peak at 10.0° corresponding to (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>. For the treated samples, the peaks at 33.4°, 37.9°, and 39.4° can be attributed to the formati-



Figure 2. The TEM and HAADF-STEM images of AHM/CNT without treatment (a and b),  $Mo_xC/CNTs$  treated at 600 °C (c and d), 700 °C (e and f), and 800 °C (g and h), respectively.

on of  $\beta$ -Mo<sub>2</sub>C under carbothermal condition.<sup>[19]</sup> This demonstrates that Mo<sub>x</sub>C/CNT catalysts are successfully prepared and the CNTs serve as the carbon source during the Mo<sub>x</sub>C formation process. These are also evidenced by the weakened intensity of the peak of CNTs with increasing temperature.

In addition to XRD analysis, XPS analysis was employed to identify the surface composition of the catalysts, and the Mo 3d spectras are shown in Figure 1b–1d. There are five different surface Mo species except  $Mo^{0+}$  in all three samples. The relative content of  $Mo^{2+}$  species increases gradually with the rise of temperature. Besides, the Mo  $3d_{5/2}$  at 229.4, 231.1, 232.3, and 233.0 eV are corresponding to  $Mo^{3+}$ ,  $Mo^{4+}$ ,  $Mo^{5+}$ , and  $Mo^{6+}$  species, respectively.<sup>[20]</sup> All of these peaks are assigned to  $MoO_xC_y$  with a wide range of binding energies referring to reference.<sup>[21]</sup>

Table 1 shows the textural properties of Mo-based catalysts determined by nitrogen physical sorption analyses. The BET surface area, pore volume, and pore size of Mo<sub>x</sub>C/CNTs decrease as the carbothermal temperature rises, resulting from the deposition of Mo-based particles on CNTs. While the carbon

loss of catalyst increases from 14, to 50, and to 70 wt% as the temperature increases from 600, to 700, and to 800° C, respetively. This is mainly caused by the formation of  $C_xH_y$  in the reduction gas  $(2xC + yH_2 \rightarrow 2C_xH_y)$  and the replacement of O species in Mo-based catalyst by C species.<sup>[19a, 20]</sup>

All Mo-based catalysts were further analyzed by TEM. As shown in Figure 2a and 2b, the initial prepared particles are dispersed on internal surfaces of the tubes for the AHM/CNTs. In the case of the Mo<sub>x</sub>C/CNTs treated at 600 °C, a large number of particles with a size range of 4-6 nm are uniformly distributed inside of CNTs (Figure 2c and 2d). When the temperature rises to 700 °C, it is observed that most particles (4-6 nm) were inside of the tubes (Figure 2e and 2f), while a few particles were distributed outside the tubes and slightly aggregated (15-22 nm, see Figure S1a). The enlarged TEM images of these particles show a d-spacing of 0.228 nm assigning to the (101) plane of the hexagonal phase of Mo<sub>2</sub>C,<sup>[20]</sup> as shown in Figure S2, proving the particles both inside and outside the CNTs being Mo<sub>2</sub>C. However, as shown in Figure 2g and 2h, the formation of Mo<sub>2</sub>C and destruction of the CNTs take place simultaneously at 800 °C. Serious aggregation of molybdenum carbide particles with



**Figure 3.** Characterization of apple wood lignin oil (extracted with DCM) with Ru/C and Mo<sub>x</sub>C/CNT 700 catalysts respectively by (a) gas chromatography-mass spectrometer and (b) gel permeation chromatography, and 2D HSQC NMR analysis of apple wood lignin oil (extracted with DCM) with (c) Ru/C catalyst and (d) Mo<sub>x</sub>C/CNT 700 catalyst respectively. X5:  $C_5$ -H<sub>5</sub> in  $\beta$ -D-xylopyranoside, X3:  $C_3$ -H<sub>3</sub> in  $\beta$ -D-xylopyranoside, X2<sub>1</sub>:  $C_1$ -H<sub>1</sub> in 2-O-acetyl- $\beta$ -D-xylopyranoside, X2<sub>1</sub>:  $C_1$ -H<sub>1</sub> in 2-O-acetyl- $\beta$ -D-xylopyranoside, X2<sub>1</sub>:  $C_1$ -H<sub>1</sub> in  $\beta$ -D-xylopyranoside, PhGI:  $C_1$ -H<sub>1</sub> in phenyl glycoside linkages. Both of apple wood lignin oils obtained from 250 °C for 3 h with 1 MPa H<sub>2</sub>.

## WILEY-VCH

particle size larger than 25 nm is also observed (Figure S1b).

# 2.1.2 Catalytic performance and structure/performance relationship of $Mo_xC/CNT$ in the lignin-first biorefinery.

The prepared  $Mo_xC/CNT$  catalysts mentioned above were then tested in the biomass catalytic reductive fractionation process to investigate the catalytic performance.

Table 2. Depolymerization of hardwood over different catalysts <sup>[a]</sup> .							
Catalyst	Carboh	Lignin	Delignifi	Mono mer (wt%)	Sugar (%)		
	(wt%)	(wt%)	(wt%)		C6	C5	
	60.6	24.4	72.9	18	99	90	
Ru/C	52.5	36.0	85.4	38	95	62	
Mo <sub>x</sub> C/CNTs 600	60.0	22.0	79.5	32	98	90	
Mo <sub>x</sub> C/CNTs 700	58.7	28.3	98.1	42	98	89	
Mo <sub>x</sub> C/CNTs 800	58.9	26.8	94.1	38	99	91	

[a] Reaction conditions: 5 g of apple wood (particle size of <40 mesh), 0.375 g of Mo<sub>x</sub>C/CNT, 200 mL of methanol, 1 MPa H<sub>2</sub> at room temperature, 250°C and 3 h. Reaction pressure is approximately 11 MPa. [b] Based on the weight of the DCM extracted fraction and Klason lignin weight (23.0 wt% in apple wood).

The catalytic reaction was carried out under the presence of H<sub>2</sub>, catalyst and methanol. The obtained lignin oil samples were subjected to GPC, GC/MS, and 2D HSQC NMR analyses. The quantification of phenolic monomers in lignin oil was obtained with the help of standard samples acquired from commercial purchase following a reference.<sup>[16a]</sup> The solid products, after separation from the catalysts, were subjected to compositional analyses.

A blank experiment without catalyst was firstly carried out. It can be found that most of the lignin fraction can be dissolved into the methanol phase even without any catalyst for hardwood. In the blank experiment, 24.4 wt% of lignin oil and 60.6 wt% of carbohydrates are obtained (entry 1, Table 2), yielding 18 wt% phenolic monomers. It should be mentioned that C6 sugar was perfectly retained and about 10% C5 sugar were lost during such treatment.

A control experiment with generally used Ru/C catalyst was also carried out. Similar to the results in literature,<sup>[9]</sup> Ru/C catalyst provide a high delignification degree (85.4 wt%), C6 retention (>95%) and high phenolic monomer yield (38 wt%). However, the carbohydrate yield and C5 sugar retention was lower than that of blank experiment, which are 52.5 wt% and 62%, respectively. This result indicating that a part of carbohydrates (mainly C5 sugar) are most likely converted to oligomeric sugars.

The catalytic performance of  $Mo_xC/CNT$  catalysts and the influence of catalyst properties on the reaction was then investigated. It can be found that  $Mo_xC/CNT$  catalysts prepared

at different temperature have different catalytic performance in lignin-first biorefinery. As shown in Figure 3a and ESI, the GC/MS detectable lignin oil composition and molecular weight distribution of lignin depolymerized over different Mo<sub>x</sub>C/CNT are very similar. The lignin oil obtained from MoxC/CNT catalysts is more complicated than that of Ru/C catalyst. It is mainly composed of guaiacol (G1-G3) and syringyl (S1-S4) lignin subunits, and some unsaturated lignin subunits (G3 and S3). In GPC analyses, there are two main signals at 220 and 500 g mol<sup>-1</sup>, indicating the depolymerization of lignin is successful, which is comparable to that of Ru/C. MoxC catalysts prepared under different temperatures have obviously different delignification degree and oil/monomer yield. As shown in Table 2, MoxC/CNT (600 °C) only provides 22.0 wt% of lignin oil, 79.5 wt% of delignification and 32 wt% of phenolic monomers. More promising results are achieved in the case of MoxC/CNT (700 °C), reaching to 28.3 wt% of lignin oil and 98.1 wt% of delignification. The yield of phenolic monomers is 42 wt%. The lignin oil yield, delignification degree and phenolic monomer yield of Mo<sub>x</sub>C/CNT (800 °C) is between the catalyst obtained at 600 °C and 700 °C.

Mo<sub>x</sub>C/CNT catalysts prepared at all temperatures provide a promising carbohydrate yield of about 60 wt% and the retention of C5 sugar around 90%, which is close to the result of blank experiment. And there is no obvious increase of acetic acid formation when compared to blank experiment. This observation could be additional evidence for the hemi-cellulose retention during the lignin depolymerization. Another importance evidence for the low sugar fraction in depolymerized oil is that the carbohydrate signals of 2D HSQC NMR analysis not exist when compared with that of Ru/C (in Figure 3c and 3d). It can be concluding that the retention of carbohydrate fractions from all Mo<sub>x</sub>C/CNTs approaching to the theoretical maximum indicates the potential of such Mo-based catalysts in hemicellulose retention. It should be noted that lignin oil yield with MoxC/CNT (28.3 wt%, 700 °C) is lower than that of Ru/C (36.0 wt%), It is believed that the increased yield of lignin oil, derived from Ru/C involved experiment, comes from the conversion of carbohydrates.

The recyclability and stability of catalyst are significant for further application. The  $Mo_xC/CNT$  catalyst was used directly in the following cycle after separation. As shown in Figure S3, the spent catalyst recycled for four runs still provide 33.5 wt% monomer yield, though slight deactivation was observed.

Based on above results, the Mo<sub>x</sub>C/CNT (700 °C) could be considered as the most promising catalyst for catalytic reductive fractionation of hard wood. The delignification and phenolic monomers yield of the Mo<sub>x</sub>C/CNT (700 °C) are better than that of benchmark Ru/C catalyst. Mo<sub>x</sub>C/CNT (700 °C) also maintains very high C5 and C6 sugar fraction. The precise depolymerization of lignin over Mo<sub>x</sub>C/CNT (700 °C) demonstrate its high selectivity in breaking the bonds between lignin and carbohydrates and the ether bonds in lignin, respectively.

The catalytic performance of  $Mo_xC/CNT$  catalysts can be connected to their characterization results. As shown in Figure 4, in such a catalytic reductive fractionation process, there are a complicated equilibrium in the reaction vessel. A catalyst can

## WILEY-VCH

accelerate certain step as induce equilibrium moving. A catalyst can quickly stabilize lignin primary fragments is very important for high lignin depolymerization degree and monomer yield. While a catalyst cannot catalyze C5 sugar decomposition is important for the high C5 retention. Characterization results indicated that Mo<sub>x</sub>C/CNT (700 °C) has high Mo<sub>x</sub>C content while keep in high dispersed state.



**Figure 4.** Schematic representation of catalytic reductive fractionation process. The biomass was fractionated into carbohydrates and depolymerized lignin fragments that were solubilized in the methanol solution without condensed lignin. Carbohydrates (containing C5 and C6 sugars) was retained.

#### 2.2 The lignin-first biorefinery of softwood over Ru/CMK-3.

The current reports about the lignin-first process are broadly characterized by using hardwood as feedstock. Unfortunately, the promising experiment obtained in hardwood cannot be straight forwarded to softwood and other biomass feedstock. Design catalyst for softwood is very important for boarding the applicable of the lignin first biorefinery process.

# 2.2.1 Catalyst design rule for softwood based on novel model compound depolymerization.

As shown in Figure 3c, there are various C-C bonds in lignin oil, indicating the C-C bond in lignin can not be depolymerized over Ru/C catalysts. Since softwood contains more C-C linkages (e.g.,  $\beta$ -5, 5-5), it is important to understand what properties are needed for softwood depolymerization.<sup>[22]</sup>

Here, a novel (5-5)-( $\beta$ -O-4)-( $\beta$ -5) tetramer in Figure 5, which was a novel model compound of lignin fragments (particularly in softwood), together with  $\beta$ -O-4 and  $\beta$ -5 model compounds were studied to understand the reactivity of various lignin linkages in the commonly used Ru/C system for the lignin-first biorefinery. The cleavage of  $\beta$ -O-4 linkage in the  $\beta$ -O-4 model compound takes place even without catalyst, as shown in Figure S4, resulting from solvolysis and thermal decomposition.

Unsurprisingly, the  $\beta$ -O-4 linkage is also broken in Ru/C catalytic systems, as shown in Figure S5. As for the  $\beta$ -5 model compound, the cleavage of a portion of  $\alpha$ -O-4 linkages is obvious without catalyst (Figure S6), and that is completely broken in Ru/C catalyst (Figure S7). However, the  $\beta$ -5 linkage is

obstinate in both cases and the depolymerized products are present as dimers. The novel (5-5)-( $\beta$ -O-4)-( $\beta$ -5) tetramer model compound was studied in Ru/C catalytic system, as shown in Figure S8. The cleavage of  $\beta$ -O-4 and  $\alpha$ -O-4 linkages takes place, while  $\beta$ -5 and 5-5 linkages are still present in the products.

As discussed above, the commonly used catalytic system (Ru/C) for the lignin-first biorefinery is ineffective to cleave the C-C bonds such as  $\beta$ -5 and 5-5 linkages, which are rich in softwood. This leads the lignin depolymerized intermediates from softwood to present as macromolecules such as phenolic dimers or oligomers. It is well known that the macromolecular intermediates easily undergo repolymerization among themselves especially with the help of acidic sites on catalyst. It thus requires a novel catalyst for the lignin-first biorefinery of softwood and other biomass feedstock rich in G type lignin, which is characterized by large pore size suitable for diffusion of the macromolecular intermediates and low acidity to reduce repolymerization reactions.



Figure 5. Synthetic routes of (a) the  $\beta$ -5 model compound and (b) the novel (5-5)-( $\beta$ -O-4)-( $\beta$ -5) tetramer model compound.

#### 2.2.2 Synthesis and characterization of Ru/CMK-3.

Based on above understanding, mesoporous carbon with no acidity was supposed to be excellent in softwood depolymerization. Hence we tested the possibility for CMK-3 as support for softwood depolymerization.

Table 3. Textural properties of various catalysts				
Samples	S <sub>BET</sub> (m²⋅ g⁻¹)	pore volume (cm <sup>3</sup> · g <sup>-1</sup> )	pore size <sup>[a]</sup> (nm)	
CMK-3	1309.87	1.449	4.31	
Ru/CMK-3	800.33	0.879	3.96	
Ru/C	648.25	0.76	-	

[a] Determined by BJH analysis and Ru/C is a typical microporous material.

CMK-3 and Ru/CMK-3 were synthesized and subjected to various analyses and compared with commercially available C and Ru/C, respectively. The small-angle XRD patterns clearly reflect the ordered mesoporous structure of CMK-3 and Ru/CMK-3 and disordered structure of C and Ru/C, as exhibited

in Figure S9a. The wide-angle XRD patterns are shown in Figure S9b. Both Ru/C and C show two strong diffraction peaks at 23° and 43°, corresponding to the (002) and (101) facets of typical graphite structure, respectively.<sup>[23]</sup> Because of the small size and high dispersion of the Ru nanoparticles, no obvious diffraction peak assigning to Ru nanoparticles can be detected from Ru/CMK-3 and Ru/C.



Figure 6. (a)  $N_2$  sorption isotherms of CMK-3, Ru/CMK-3 and Ru/C catalysts and (b)  $NH_3\mbox{-}TPD$  profiles of Ru/C and Ru/CMK-3 catalysts.



Figure 7. TEM images of CMK-3 (a and b), Ru/CMK-3 (c and d), and Ru/C (e and f). The images of d and f are HAADF-STEM ones.

The ordered mesoporous structures of CMK-3 and Ru/CMK-3 were further confirmed by nitrogen physical sorption analysis. As shown in Figure 6a, both CMK-3 and Ru/CMK-3 show a type IV isotherm with a characteristic hysteresis loop in the relative pressure range of 0.4 to 0.9, indicating mesoporous materials. The BET specific surface area of CMK-3 used in this study is about 1309.87 m<sup>2</sup>/g, and the average pore size measured by BJH method is 4.31 nm, as listed in Table 3. After the introduction of Ru, the specific surface area and the average

pore size decrease to 800.33 m<sup>2</sup>/g and 3.96 nm, respectively. This is likely due to the deposition of the metal ruthenium nanoparticles into the pores. But they are still significantly larger than those from Ru/C. The larger pore volume and pore size of Ru/CMK-3 is benefit to the diffusion of the macromolecules and thus reduces their repolymerization.

Figure 7 shows the TEM images of a CMK-3, Ru/CMK-3 and Ru/C samples. TEM images certify the presence of pore structure and type of mesoporous material. It can be seen that CMK-3 maintains a good two-dimensional hexagonal structure (Figure 7a for horizontal direction and Figure 7b for vertical direction), indicating that CMK-3 has typical ordered mesoporous structure and parallel pores.<sup>[23a]</sup> The TEM images of Ru/CMK-3 clearly show that the metallic Ru is well dispersed on the surface of the carbon material and the particle size of Ru is about 2–4 nm (Figure 7c and 7d). It also shows that there is no significant change in the ordered mesoporous morphology after the introduction of metallic nanoparticles. In the case of Ru/C catalyst, Ru nanoparticles are slightly aggregated as shown in Figure 7e and 7f.

The NH<sub>3</sub>-TPD profiles of Ru/CMK-3 and Ru/C are exhibited in Figure 6b. In general, the NH<sub>3</sub>-TPD desorption peak at 200 °C is attributed to the chemical desorption of NH<sub>3</sub> from weak acidic sites. The intensity of the desorption peak from Ru/C is much stronger than that from Ru/CMK-3 at around 200 °C, suggesting the weaker acidity of Ru/CMK-3.

#### 2.2.3 Depolymerization of softwood over Ru/CMK-3.

As discussed above, Ru/CMK-3 is characterized by mesoporous structure and weaker acidity in comparison to Ru/C, both of which can reduce the repolymerization reaction among reactive macromolecular intermediates. The catalytic performance of Ru/CMK-3 was thus studied in the lignin-first biorefinery of softwood and compared with the result from Ru/C.

Table 4. Depolymerization of pine wood over different catalysts <sup>[a]</sup> .					
Catalyst	Carbohydrate (wt%)	Lignin oil yield (wt%)	Delignific ation <sup>[b]</sup> (wt%)	Monomer (wt%)	
Ru/C	55.3	27.9	61.7	16.3	
Ru/CMK-3	52.9	35.3	85.8	20.0	

[a] Reaction conditions: 0.5 g of softwood (particle size of <40 mesh), 0.0375 g of catalyst, 20 mL of methanol, 1 MPa H<sub>2</sub> at room temperature, 250 °C and 3 h. Reaction pressure is approximately 10 MPa. [b] Based on the weight of the DCM extracted fraction and Klason lignin weight (27.0 wt% in pine).

In this research, Ru/CMK-3 provides 35.3 wt% of lignin oil yield, 85.8 wt% of delignification, and 20.0 wt% monomer yield, all of which are higher than those from Ru/C (27.9 wt%, 61.7 wt %, and 16.3 wt%, respectively), as listed in Table 4. However, the lignin oil obtained from Ru/CMK-3 catalyst composed mostly of propylguaiacol (G2) followed by ethylguaiacol (G1) and allylg-



## WILEY-VCH



**Figure 8.** Characterization of pine wood lignin oil (extracted with DCM) with Ru/C and Ru/CMK-3 catalysts respectively by (a) gas chromatography-mass spectrometer and 2D HSQC NMR analysis of pine wood lignin oil (extracted with DCM) with (b) Ru/C catalyst and (c) Ru/CMK-3 catalyst respectively. X5: C<sub>5</sub>-H<sub>5</sub> in  $\beta$ -D-xylopyranoside. Both of pine wood lignin oils obtained from 250 °C for 3 h with 1 MPa H<sub>2</sub>.

uaiacol (G3), which has nearly same product distribution compared to Ru/C in Figure 8a analyzed by GC-MS. As shown in Figure S10, It is worth noting that the 5-5 and  $\beta$ -5 linkages are still present in the products from the depolymerisation of the novel (5-5)-(β-O-4)-(β-5) tetramer model compound with Ru/CMK-3, indicating that the increases in lignin oil yield and delignification are not derived from the cleavage of C-C linkages. This result is further supported by 2D HSQC NMR analysis of lignin oil obtained from pine wood using Ru/CMK-3 catalyst. Various  $\beta$ -5 linkages and  $\beta$ - $\beta$  linkages still exist in lignin oil in Figure 8c. A reasonable explanation of this circumstance can be proposed as that the macromolecular intermediates containing C-C linkages obtained from lignin depolymerization are promptly diffused and stabilized as liquid product in the mesopores of Ru/CMK-3, and the weak acidity of Ru/CMK-3 further prevent the repolymerization of the intermediates. This is proved by the GPC analysis of two lignin oils that the molecular weights of lignin oil from Ru/CMK-3 (Mw=918 g/mol; Mn=485 g/mol) are significantly larger than those from Ru/C (Mw=644 g/mol: Mn=287 g/mol). Meanwhile, Ru/CMK-3 catalyst has high recycling stability. The spent catalyst was used directly in the following cycle. As shown in Figure S11, the monomer yields still remain 16.5 wt% after four recycling runs. This result proves the good recycle ability in catalytic lignocellulosic biomass fraction.

The results presented above indicate that the Ru/CMK-3 catalyst is very promising for the depolymerization of softwood lignin due to the combination of mesoporosity and limited acidity. Such a catalyst could be further extend to the depolymerization of other G type lignin rich feedstock such as grass as detailed in ESI.

## 3. Conclusions

Based on the above consideration, a flexible lignin-first biorefinery could be developed by task specific catalyst design in terms of hemicellulose retention or feedstock extension. In the case of hardwood which contains a high S/G ratio of lignin building block, the retention of hemicellulose in solid product is of great importance for bioconversion of C5 and C6 sugars. Mo<sub>x</sub>C/CNT prepared by carbothermal reduction is found to be a promising catalyst for cleavage of the bonds between lignin and carbohydrates with high selectivity and also a robust catalyst for lignin depolymerization. In the case of softwood, low yield of the lignin oil in the currently developed lignin-first biorefinery is the main problem due to the abundance of C-C linkages such as β-5 and 5-5 bonds and the difficulty in cleavage of those bonds. Extension of the feedstock for the lignin-first biorefinery from hardwood to softwood is very important because softwood contains higher lignin content than hardwood. To increase the lignin oil yield from softwood, it does not necessarily require the cleavage of C-C linkages. Stabilization of the macromolecular intermediates by prompt diffusion and hydrogenation is another option. Ru/CMK-3, characterized by weak acidity and high mesoporosity, is proved to be a potential catalyst in the ligninfirst biorefinery of softwood.

## 4. Experimental Section

#### 4.1 Materials.

The lignocelluloses biomasses (apple wood, pine wood and wheat straw) used in this study were grounded to less than 40 mesh and dried at 80 °C for 24 h. Commercial Ru/C (5%) catalyst, activated carbon, pluronic (P123), triblock polymer (average molecular weight 5800), triblock surfactant F127, tetraethyl orthosilicate (TEOS), acetone-d<sub>6</sub>, ruthenium trichloride (99%) and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> (99%) were purchased from Sigma-Aldrich. Raney Ni, sucrose, isoeugenol, 1-([1,1'-biphenyl]-4-yl) ethanone were provided by Aladdin Chemical Reagent Co. Ltd. Carbon nanotubes (CNTs) were purchased from Sinopharm Chemical Reagent Co. Ltd. K<sub>2</sub>CO<sub>3</sub>, hydrochloric acid, sulfuric acid, methanol, ethanol, acetone, isopropanol, urea peroxide, horseradish peroxidase, pyridinium tribromide, cyclohexane, ethyl acetate, dimethyl formamide and dichloromethane (DCM) were provided by J&K Scientific. All the chemicals were used without further purification.

#### 4.2 Synthesis and characterization of model compounds.

The  $\beta\text{-}O\text{-}4$  model compound of lignin used in this research was synthesized according to the reported methods.  $^{[16a]}$ 

β-5 model compound (**B**) was synthesized starting from a commercially available compound isoeugenol (**A**) in Figure 5. In detail, 5.0 g of **A** was dissolved in an acetone/water (125/200 mL) solution with magnetic stirring. 1.8 g of urea peroxide and 10.0 mg of horseradish peroxidase were then added to the solution and stirred for 1 h at room temperature until **A** was reacted completely (TLC control). The reaction solution was subsequently acidified with 1 N hydrochloric acid to pH being around 3 and extracted by ethyl acetate. The extract was dried with anhydrous sodium sulfate and evaporated under vacuum to remove the solvent. The resulting product was then further purified by column chromatography with cyclohexane/ethyl acetate (6/1, v/v) as mobile phase. After evaporation of the solvent under vacuum, the purified **B** with a yield of 32.0% was finally obtained.

The synthetic route of novel (5-5)-(β-O-4)-(β-5) tetramer model compound is presented in Figure 5. 10.0 g commercially available C was dissolved in ethyl acetate and brominated with pyridinium tribromide (17.9 g) at room temperature for 2 h. After completion of the reaction (TLC control), the mixture was dissolved in deionized water and then extracted with ethyl acetate. The organic phase was separated and dried with anhydrous sodium sulfate. After evaporation of the solvent under vacuum and recrystallization in methanol, compound D with a yield of 25.8% was obtained as a brown crystal. 3.9 g of **D** and 3.6 g of **B** were then dissolved in DMF and reacted at 80 °C for 4 h using K<sub>2</sub>CO<sub>3</sub> (2.7 g) as catalyst. After dissolving the mixture with deionized water, extracting the organics with ethyl acetate, drying the organic phase with anhydrous sodium sulfate, and evaporating the solvent, a red oil was obtained. The red oil was further purified by column chromatography with cyclohexane/ethyl acetate (8/1, v/v) as mobile phase. After evaporation of the solvent under vacuum, the tetramer E with a yield of 37.8% was finally obtained.

#### 4.3 Preparation of Mo<sub>x</sub>C/CNTs catalyst.

The CNTs support, in the range of 40–60 mesh, was dried at 110 °C for 3–4 h to remove moisture prior to use. The Mo<sub>x</sub>C/CNTs catalysts were synthesized by incipient wetness impregnation. Briefly, the aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> (10 mL) were added to the CNTs support (3 g) slowly with stirring, achieving a 10 wt% Mo loading. Then, the mixture was put into an ultrasonic bath for 60 min at room temperature. The resulting mixture was dried at 100 °C overnight. The carbide species of

Mo was prepared by carbothermal reduction treatment. About 1.5 g sample ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>/CNTs) was put into a tubular furnace for calcination under H<sub>2</sub> atmosphere each time. The temperature increased at a rate of 1 °C/min from 25 °C to reduction temperature (i.e., 600, 700 and 800 °C) and then held at the reduction temperature for 60 min. After the sample cooled to room temperature under N<sub>2</sub> atmosphere, treatment in a flow of 1% O<sub>2</sub>/He for 60 min to passivate the surface of carbide species was performed.

#### 4.4 Preparation of Ru/CMK-3 catalyst.

The support CMK-3 was firstly prepared using SBA-15 silica (synthesized following a reference) as the template and sucrose as the carbon source.<sup>[24]</sup> 1.0 g of SBA-15 powder was added to a solution which contained 1.3 g of sucrose and 5.0 g of deionized water. Then 0.1 mL of concentrated sulfuric acid was added to the solution and incubated at 100 °C for 6 h and subsequently at 160 °C for 6 h. Another solution including 0.8 g of sucrose, 0.05 mL of concentrated sulfuric acid, and 5.0 g of deionized water was added to the resulting solid and heated again at 100 and 160 °C for 6 h each, same as the previous steps. The solid was finally carbonized at 900 °C for 2 h under N<sub>2</sub> and washed with 5 wt% HF for removing silicon. The prepared CMK-3 was deposited by 5 wt% Ru in an incipient-wetness impregnation method. The RuCl<sub>3</sub> was used as the precursor for the catalyst. Following the impregnation, the solid was dried at 100 °C overnight and calcined under a H<sub>2</sub> atmosphere at 400 °C for 3 h.

#### 4.5 Characterization methods.

X-ray diffraction (XRD) experiments were carried out on a Bruker diffractometer with Cu K $\alpha$  radiation (40 kV, 120 mA), and data were obtained in both small and wide angle. The angular step size was 0.05° and the counting time was 8 s per step.

Transmission electron microscopy (TEM) was obtained with Philips Techai G2 microscope and operated at 200 kV. The samples dispersed in ethanol were deposited on copper grid before measurement.

Nitrogen adsorption-desorption isotherms were determined on a Micromeritics ASAP 2020 HD 88 surface area and porosity analyzer. The samples were firstly degassed at 623 K in a vacuum of  $1.33 \times 10^{-3}$  Pa, and Brunauer–Emmett–Teller (BET) theory was used in surface area determination.

X-ray photoelectron spectroscopy (XPS) spectra were acquired by ESCALAB 250 spectrometer equipped with an Al K $\alpha$  source. Deconvolutions analysis were delivered by XPS Peak 4.1 software. The C 1s peak at 284.6 eV was taken as reference to calibrate binding energies and account for charging effects.

The liquid product was analyzed by GC-MS (Agilent 7890A/5975C system) equipped with a HP-5 column (30 m × 0.25 mm). The temperature program of the oven was starting at 50 °C with a 1 min holdup, ramping to 300 °C at a rate of 5 °C/min, and holding at 300 °C for 4 min. The analysis of the mass spectra was mainly based on an automatic library search (NIST11, version 2.0). Elemental analysis was determined using a Vario EL III elemental analyzer. 0.1g carbohydrate pulp was treated with 1 ml 72 wt% H<sub>2</sub>SO<sub>4</sub> for 1 h and heated to 120 °C for 1 h after adding 28 ml water. The sugar or carboxylic acid (aqueous phase) content was determined by Thermo U-3000 high performance liquid chromatography (HPLC) using UV detector and an Aminex HPX-87H or fast acid analysis chromatographic column.

Ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) was by Autochem 2910 II from Micromeritics. Ru/CMK-3 (0.1 g) and Ru/C samples (0.1 g) were pre-treated at 400 °C for 2 hours under a stream of He (20 cm<sup>3</sup>/min). After that, the catalyst was adsorbed at 200 °C for 30 min in a mixed gas of NH<sub>3</sub> and He (20 cm<sup>3</sup>/min) with an ammonia gas concentration of 10%, and then the sample was purged with He for 1 h at

the same temperature. Finally, the desorption of NH<sub>3</sub> was monitored at a heating rate of 10 °C/min at a temperature range of 200–700 °C.

2D HSQC NMR spectra was acquired on a Bruker AVANCE 600 MHz spectrometer at 25 °C using acetone-d<sub>6</sub>. The experiments were performed from 20 ppm in <sup>1</sup>H dimension with 2048 data points (acquisition time 128 ms) and 219 ppm in <sup>13</sup>C dimension with 512 increments (acquisition time 11.6 ms). Assignment of typical carbohydrate and lignin signals follow a reference. <sup>[25]</sup>

GPC analysis was conducted at 35 °C on a Waters HPLC 1525 equipped with Waters Styragel HR 4E THF and Waters Styragel HR 5E THF column (4.6 x 300 mm), using THF as the solvent (1 mL/min) and UV detection at 240 nm. The sample of lignin oil extracted with DCM (30 mg) was dissolved in tetrahydrofuran (THF, 2 mL) and subsequently filtered with a 0.2  $\mu$ m PTFE membrane. The molecular weight was calibrated using polystyrene standards.

# 4.6 Catalytic hydrotreatment of model compounds and lignocellulosic biomass.

The catalytic delignification of lignocellulosic biomass and lignin model compounds were carried out in high pressure autoclave with a mechanical stirrer. Typically, the autoclave was charged with catalyst, biomass or model compounds, and relevant solution. The reactor was purged and pressurized at room temperature as required and heated to a design temperature (220-250 °C) for 3 h. Then, the reactor was cooled to room temperature. For the biomass, the resulting mixture was filtered to obtain lignin oil and carbohydrate pulp. The carbohydrate pulp was dried in an oven and the lignin oil was further treated by DCM-water extraction to get DCM phase and aqueous phase respectively. The delignification degree was determined based on the DCM soluble oil weight and Klason lignin weight. Catalysts separated from the carbohydrate pulp were used in following cycle, as the procedure described by Bosch et al. with few modifications. [9] The liquid mixture obtained from lignin model compounds was filtered and analyzed directly after evaporation using GC-MS. All of the experiments were detailed in Electronic Supporting Information (ESI).

### Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant number U1663227)

**Keywords:** lignin-first biorefinery• hemicellulose retention • soft wood• catalytic reductive fractionation• mesoporous carbon

- a) H. Zhu, W. Luo, P. N. Ciesielski, Z. Fang, J. Y. Zhu, G. Henriksson, M. E. Himmel, L. Hu, *Chem. Rev.* 2016, *116*, 9305-9374; b) X. Zhao, H. Zhou, V. S. Sikarwar, M. Zhao, A.-H. A. Park, P. S. Fennell, L. Shen, L.-S. Fan, *Energy Environ. Sci.* 2017, *10*, 1885-1910; c) R. Behling, S. Valange, G. Chatel, *Green Chem.* 2016, *18*, 1839-1854.
- a) D. M. Alonso, S. H. Hakim, S. Zhou, W. Won, O. Hosseinaei, J. Tao, V. Garcia-Negron, A. H. Motagamwala, M. A. Mellmer, K. Huang, C. J. Houtman, N. Labbé, D. P. Harper, C. T. Maravelias, T. Runge, J. A. Dumesic, *Sci. Adv.* 2017, 3, e1603301; b) J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger, J. A. Dumesic, *Science* 2014, *343*, 277-280; c) J. Q. Bond, A. A. Upadhye, H. Olcay, G. A. Tompsett, J. Jae, R. Xing, D. M. Alonso, D. Wang, T. Zhang, R. Kumar, A. Foster, S. M. Sen, C. T. Maravelias, R. Malina, S. R. H. Barrett, R. Lobo, C. E. Wyman, J. A. Dumesic, G. W. Huber, *Energy Environ. Sci.* 2014, *7*, 1500-1523; d) J. C. Serrano-Ruiz, J. A. Dumesic, *Energy Environ. Sci.* 2011, *4*, 83-99; e) I. Delidovich, P.

J. Hausoul, L. Deng, R. Pfutzenreuter, M. Rose, R. Palkovits, *Chem. Rev.* **2016**, *116*, 1540-1599; f) J. C. Serrano-Ruiz, J. A. Dumesic, *Energy Environ. Sci.* **2011**, *4*, 83-99.

- [3] a) V. B. Agbor, N. Cicek, R. Sparling, A. Berlin, D. B. Levin, *Biotechnol. Adv.* 2011, 29, 675-685; b) C. S. Lancefield, I. Panovic, P. J. Deuss, K. Barta, N. J. Westwood, *Green Chem.* 2017, 19, 202-214.
- [4] a) M. J. Negro, P. Manzanares, J. M. Oliva, I. Ballesteros, M. Ballesteros, *Biomass Bioenergy* 2003, *25*, 301-308; b) C. Li, B. Knierim, C. Manisseri, R. Arora, H. V. Scheller, M. Auer, K. P. Vogel, B. A. Simmons, S. Singh, *Bioresour. Technol.* 2010, *101*, 4900-4906; c) F. Carrillo, M. J. Lis, X. Colom, M. López-Mesas, J. Valldeperas, *Process Biochem.* 2005, *40*, 3360-3364; d) X. Zhao, K. Cheng, D. Liu, *Appl. Microbiol. Biotechnol.* 2009, *82*, 815; e) L. da Costa Sousa, M. Jin, S. P. S. Chundawat, V. Bokade, X. Tang, A. Azarpira, F. Lu, U. Avci, J. Humpula, N. Uppugundla, C. Gunawan, S. Pattathil, A. M. Cheh, N. Kothari, R. Kumar, J. Ralph, M. G. Hahn, C. E. Wyman, S. Singh, B. A. Simmons, B. E. Dale, V. Balan, *Energy Environ. Sci.* 2016, *9*, 1215-1223; f) J. S. Kim, Y. Y. Lee, T. H. Kim, *Bioresour. Technol.* 2016, *199*, 42-48; g) Q. Yu, J. Liu, X. Zhuang, Z. Yuan, W. Wang, W. Qi, Q. Wang, X. Tan, X. Kong, *Bioresour. Technol.* 2016, *199*, 265-270.
- [5] a) L. J. Jonsson, C. Martin, *Bioresour. Technol.* 2016, 199, 103-112; b)
   L. Shuai, J. Luterbacher, *ChemSusChem* 2016, 9, 133-155.
- [6] Y. Huang, Y. Duan, S. Qiu, M. Wang, C. Ju, H. Cao, Y. Fang, T. Tan, Sustainable Energy Fuels 2018, 2, 637-647.
- [7] P. Ferrini, R. Rinaldi, Angew. Chem. Int. Ed. 2014, 53, 8634-8639.
- [8] T. Parsell, S. Yohe, J. Degenstein, T. Jarrell, I. Klein, E. Gencer, B. Hewetson, M. Hurt, J. I. Kim, H. Choudhari, B. Saha, R. Meilan, N. Mosier, F. Ribeiro, W. N. Delgass, C. Chapple, H. I. Kenttämaa, R. Agrawal, M. M. Abu-Omar, *Green Chem.* **2015**, *17*, 1492-1499.
- S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan, B. F. Sels, *Energy Environ. Sci.* 2015, *8*, 1748-1763.
- [10] a) E. M. Anderson, M. L. Stone, M. J. Hülsey, G. T. Beckham, Y. Román-Leshkov, ACS Sustainable Chemistry & Engineering 2018, 6, 7951-7959; b) E. M. Anderson, M. L. Stone, R. Katahira, M. Reed, G. T. Beckham, Y. Román-Leshkov, Joule 2017, 1, 613-622; c) X. Ouyang, X. Huang, B. M. S. Hendriks, M. D. Boot, E. J. M. Hensen, Green Chemistry 2018, 20, 2308-2319; d) M. V. Galkin, J. S. Samec, ChemSusChem 2014, 7, 2154-2158; e) X. Huang, O. M. Morales Gonzalez, J. Zhu, T. I. Korányi, M. D. Boot, E. J. M. Hensen, Green Chemistry 2017, 19, 175-187; f) H. Luo, I. M. Klein, Y. Jiang, H. Zhu, B. Liu, H. I. Kenttämaa, M. M. Abu-Omar, ACS Sustainable Chemistry & Engineering 2016, 4, 2316-2322; g) Z. Cao, M. Dierks, M. T. Clough, I. B. Daltro de Castro, R. Rinaldi, Joule 2018, 2, 1118-1133; h) I. Graça, R. T. Woodward, M. Kennema, R. Rinaldi, ACS Sustainable Chemistry & Engineering 2018, 6, 13408-13419.
- [11] a) W. Schutyser, T. Renders, S. Van den Bosch, S. F. Koelewijn, G. T. Beckham, B. F. Sels, *Chem. Soc. Rev.* 2018, *47*, 852-908; b) M. V. Galkin, J. S. Samec, *ChemSusChem* 2016, *9*, 1544-1558.
- [12] D. Mohan, C. U. Pittman, P. H. Steele, *Energy Fuels* **2006**, *20*, 848-889.
   [13] J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen,
- J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* 2010, 110, 3552-3599.
- [14] a) T. Renders, S. Van den Bosch, S. F. Koelewijn, W. Schutyser, B. F. Sels, *Energy & Environmental Science* 2017, *10*, 1551-1557; b) L. Soh, J. Curry, E. J. Beckman, J. B. Zimmerman, ACS Sustainable Chemistry & Engineering 2013, *2*, 387-395; c) C. Chesi, I. B. D. de Castro, M. T. Clough, P. Ferrini, R. Rinaldi, *ChemCatChem* 2016, *8*, 2079-2088; d) M. V. Galkin, A. T. Smit, E. Subbotina, K. A. Artemenko, J. Bergquist, W. J. J. Huijgen, J. S. M. Samec, *ChemSusChem* 2016, *9*, 3280-3287; e) M. L. Stone, E. M. Anderson, K. M. Meek, M. Reed, R. Katahira, F. Chen, R. A. Dixon, G. T. Beckham, Y. Román-Leshkov, ACS Sustainable Chemistry & Engineering 2018, *6*, 11211-11218; f) W. J. Sagues, H. Bao, J. L. Nemenyi, Z. Tong, ACS Sustainable Chemistry & Engineering 2018, *6*, 4958-4965.

- [15] a) W.-S. Lee, Z. Wang, R. J. Wu, A. Bhan, *J. Catal.* 2014, *319*, 44-53;
  b) H. Ren, W. Yu, M. Salciccioli, Y. Chen, Y. Huang, K. Xiong, D. G. Vlachos, J. G. Chen, *ChemSusChem* 2013, *6*, 798-801; c) R. Ma, W. Hao, X. Ma, Y. Tian, Y. Li, *Angew. Chem. Int. Ed.* 2014, *53*, 7310-7315;
  d) R. Ma, K. Cui, L. Yang, X. Ma, Y. Li, *Chem. Commun.* 2015, *51*, 10299-10301.
- [16] a) L.-P. Xiao, S. Wang, H. Li, Z. Li, Z.-J. Shi, L. Xiao, R.-C. Sun, Y. Fang, G. Song, ACS Catal. 2017, 7, 7535-7542; b) C.-J. Chen, W.-S. Lee, A. Bhan, Appl. Catal. A 2016, 510, 42-48; c) K. Murugappan, C. Mukarakate, S. Budhi, M. Shetty, M. R. Nimlos, Y. Román-Leshkov, Green Chem. 2016, 18, 5548-5557; d) R. Ma, W. Hao, X. Ma, Y. Tian, Y. Li, Angew. Chem. Int. Ed. 2014, 53, 7310-7315.
- [17] a) R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. Bruijnincx, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* 2016, *55*, 8164-8215; b) T. Renders, S. Van den Bosch, S. F. Koelewijn, W. Schutyser, B. F. Sels, *Energy Environ. Sci.* 2017, *10*, 1551-1557.
- [18] a) M. P. Pandey, C. S. Kim, *Chem. Eng. Technol.* 2011, *34*, 29-41; b)
   W. Zhao, L.-P. Xiao, G. Song, R.-C. Sun, L. He, S. Singh, B. A. Simmons, G. Cheng, *Green Chemistry* 2017, *19*, 3272-3281.

- [19] a) F. Yang, K. Sliozberg, H. Antoni, W. Xia, M. Muhler, *Electroanalysis* **2016**, *28*, 2293-2296; b) X. Li, D. Ma, L. Chen, X. Bao, *Catal. Lett.* **2007**, *116*, 63-69.
- [20] H. Wang, S. Liu, K. J. Smith, Energy Fuels 2016, 30, 6039-6049.
- [21] M. Shetty, K. Murugappan, T. Prasomsri, W. H. Green, Y. Román-Leshkov, J. Catal. 2015, 331, 86-97.
- [22] C. Li, X. Zhao, A. Wang, G. W. Huber, T. Zhang, Chem. Rev. 2015, 115, 11559-11624.
- [23] a) W. Yin, Z. Tang, R. H. Venderbosch, Z. Zhang, C. Cannilla, G. Bonura, F. Frusteri, H. J. Heeres, ACS Catalysis 2016, 6, 4411-4422;
  b) Q. Xie, A. Zheng, S. Zhai, S. Wu, C. Xie, Y. Zhang, Y. Guan, J. Solid State Electrochem. 2015, 20, 449-457.
- [24] S. Manet, J. Schmitt, M. Impéror-Clerc, V. Zholobenko, D. Durand, C. L. P. Oliveira, J. S. Pedersen, C. Gervais, N. Baccile, F. Babonneau, I. Grillo, F. Meneau, C. Rochas, *J. Phys. Chem.* **2011**, *115*, 11330-113.
- [25] T. Q. Yuan, S. N. Sun, F. Xu, R. C. Sun, J Agric Food Chem 2011, 59, 10604-10614.

## WILEY-VCH

## Entry for the Table of Contents (Please choose one layout)

## FULL PAPER



A flexible lignin-first biorefinery could be developed by task specific catalyst design in terms of hemicellulose retention or feedstock extension. Mo<sub>x</sub>C/CNT is found to be a promising catalyst for the retention of hemicellulose by cleavage of the bonds between lignin and carbohydrates with high selectivity. Ru/CMK-3 achieve the extension of the feedstock for the lignin-first biorefinery from hardwood to softwood

S. Qiu, X. Guo, Y. Huang, Y. Fang\*, T. Tan

## Page No. – Page No.

Task-Specific Catalyst Development for Lignin-First Biorefinery toward Hemicellulose Retention or Feedstock Extension