

Tungsten Carbide: A Remarkably Efficient Catalyst for the Selective Cleavage of Lignin C–O Bonds

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A remarkably effective method for the chemoselective cleavage of the C–O bonds of typical β -O-4 model compounds and the deconstruction of lignin feedstock was developed by using tungsten carbide as the catalyst. High yields of C-O cleavage products (up to 96.8%) from model compounds and liquid oils (up to 70.7%) from lignin feedstock were obtained under low hydrogen pressure (0.69 MPa) in methanol. The conversion efficiency was determined to a large extent by solvent effects and was also affected by both the electronic and steric effects of the lignin model compounds. In situ W2C/activated carbon (AC)-catalyzed hydrogen transfer from methanol to the substrate was proposed to be responsible for the high performance in methanol solvent. The conversion of 2-(2-methoxyphenoxy)-1-phenylethanol showed that the catalyst could be reused five times without a significant loss in activity for C-O bond cleavage, whereas the selectivity to value-added styrene increased markedly owing to partial oxidation of the W₂C phase according to X-ray diffraction, Raman spectroscopy, and transmission electron microscopy characterization. 2D-HSQC-NMR spectroscopy analysis showed that W₂C/AC exhibited high activity not only for β -O-4 cleavage but also for the deconstruction of more resistant α -O-4 and β - β linkages, so that a high yield of liquid oil was obtained from lignin. Corn stalk lignin was more liable to be depolymerized than birch lignin owing to its loosened structure (scanning electron microscopy results), larger surface area (BET results), and lower molecular weight (gel-permeation chromatography results), whereas its liquid oil composition was more complicated than that of birch wood lignin in that the former lignin contained more *p*-hydroxyphenyl units and the former contained noncanonical units.

Introduction

Lignocellulose is the most abundant form of biomass that has the potential to serve as a sustainable feedstock to replace fossil resources for the production of future chemicals and biofuels.^[1] As one of the three major components in lignocellulose, lignin accounts for 10–35% by weight and up to 40% by energy of lignocellulosic biomass, and the conversion of lignin into value-added products will greatly improve the economics of the overall biorefinery process.^[2] However, in comparison with the other two components (i.e., cellulose and hemicellu-

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lose) of lignocellulosic materials, lignin is a more complicated three-dimensional amorphous polymer consisting of methoxylated phenylpropanoid units of various types and is relatively intractable.^[3] It is typically regarded as a low-value byproduct in most current biorefinery processes. Considering the aromatic features of lignin, recent advances have demonstrated the potential for the conversion of lignin into a spectrum of aromatic compounds by catalysis, and these aromatics may serve as alternatives to traditional aromatic compounds obtained from fossil resources.^[2,4]

Among the various reported strategies for the chemical disassembly of lignin, $^{\scriptscriptstyle[5]}$ one of the most popular and efficient approaches is hydrocracking by using supported noble metals such as Ru,^[6] Pd,^[7] Pt,^[8] Rh,^[9] Au,^[10] and Re^[11] as catalysts. In lignin systems, the aryl C-O bonds are not very active, and high temperatures and high hydrogen pressures are usually required for their cleavage. The harsh reaction conditions, in turn, lead to undesired concurrent hydrogenation of the aromatic rings and cleavage of aliphatic C-O bonds, which afford a mixture of low depolymerized lignin products, phenols, cyclanes, and some other repolymerization products. A major challenge is the selective cleavage of the aryl C-O bond rather than overhydrogenation of the aromatic ring.^[12] Moreover, owing to the scarcity and high costs of noble metals, it is highly desirable to develop cheap and efficient catalysts for the production of aromatics from lignin.

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Carbides can be formed by carburizing metals from groups 4-6, which are much cheaper than noble metals, but they show catalytic performances similar to those of platinumgroup metals in a variety of reactions involving hydrogenation.^[13] Inspired by this property, we first reported that nickel promoted tungsten carbide supported on active carbon (Ni-W₂C/AC) could replace noble metals to catalyze selective C-C cleavage of cellulose to ethylene glycol through consecutive retro-aldol and hydrogenation reactions.^[14] Building on the above results, we further found that Ni-W₂C/AC could catalyze the direct hydrocracking of raw woody biomass into two groups of chemicals, namely, diols from the carbohydrate fraction and monophenols from the lignin fraction.^[15] Though this bimetallic catalyst exhibited competitive activity relative to that of noble metal catalysts, the precise role of tungsten carbide in the hydrocracking of lignin is still unclear, particularly the pathway for cleavage of the C-O bond in lignin. In this paper, starting from 2-(2-methoxyphenoxy)-1-phenylethanol, a typical lignin model compound, we report the selective cleavage of the C–O bonds in β -O-4 lignin model compounds by using tungsten carbide as the catalyst without the addition of a second metal and extension to the catalytic conversion of realistic lignin. This catalytic process features low hydrogen pressure and high aromatic selectivity without destroying the aromatic rings in the cleavage of the C-O bonds in both lignin feedstocks and model compounds.

Results and Discussion

Preliminary study with β -O-4 model compound

2-(2-Methoxyphenoxy)-1-phenylethanol (1), a common β -O-4 dimeric model compound of lignin, was first investigated to explore the activity of W₂C/AC for the cleavage of C–O bonds. It was found that in all trials (Table 1), compound 1 was converted into styrene, ethylbenzene, and guaiacol as the dominant products in methanol solvent under a low hydrogen pressure (Scheme 1). The catalytic activity and the selectivity to the products highly depended on the reaction temperature. A low temperature (200°C) led to low conversion (23.3%) with styrene and guaiacol as the primary products (Table 1, entry 1), and the yield of ethylbenzene was only 2.3%. Upon increasing the reaction temperature (Table 1, entries 1-5), not only the conversion of the substrate but also the yield of ethylbenzene remarkably increased. For instance, compound 1 was nearly completely consumed at 260 °C in 2 h and afforded ethylbenzene and guaiacol in yields up to 88.4 and 93.0%, respectively (Table 1, entry 4). The total yield of ethylbenzene plus styrene (E+S) was 96.8% at this temperature. Upon performing the reaction at 280 °C, the highest yield of ethylbenzene (91.9%) and

Table 1. Hydrogenolysis of 2-(2-methoxyphenoxy)-1-phenylethanol catalyzed by W ₂ C/AC under different reaction conditions. ^[a]							
Entry	Temp. [°C]	Conv. ^[b] [%]	Yield [%] ^[b] ethylbenzene	styrene	$E + S^{[c]}$	guaiacol	
1	200	23.3	2.3	16.0	18.3	17.4	
2	220	54.2	3.1	38.5	41.6	39.8	
3	240	97.3	23.6	59.8	83.4	83.7	
4	260	99.8	88.4	8.5	96.8	93.0	
5	280	100	91.9	1.6	93.5	89.5	
6 ^[d]	260	100	46.5	46.2	92.7	89.2	
7 ^[e]	260	43.9	7.1	11.4	18.5	6.9	
8 ^[f]	240	100	53.5	24.3	77.8	75.1	

[a] Reactions conditions: unless otherwise specified, a stainless-steel autoclave was charged with the substrate (100 mg), 30 wt% W₂C/AC (100 mg), and methanol (30 mL), and the vessel was pressurized with H₂ (0.69 MPa); the reactions were performed at different temperatures for 2 h. [b] The conversion of 2-(2-methoxyphenoxy)-1-phenylethanol and yields of the products were determined by GC-FID with mesitylene as an internal standard. [c] E+S is the abbreviation of ethylbenzene plus styrene. [d] 30 wt% W₂C/AC (50 mg) was used. [e] No catalyst was employed; considerable amounts of etherification products, dipolymers, and other byproducts were detected. [f] H₂ (4 MPa) was the initial pressure.

the lowest yield of styrene (1.6%) were obtained (Table 1, entry 5). Apparently, the selectivity to ethylbenzene/styrene was thoroughly reversed relative to that observed at low temperatures. The shift in selectivity from styrene to ethylbenzene indicates that higher temperatures favor hydrogenation of the alkene group in styrene. Increasing the catalyst amount (Table 1, entry 4 vs. 6) and the hydrogen pressure (Table 1, entry 3 vs. 8) also benefitted the hydrogenation reaction. On the whole, the yields of the C–O bond-cleavage products (E +S and guaiacol) were higher than 83% with almost complete conversion (>97%) if the temperature was over 240°C. In sharp comparison, thermal reaction without a catalyst at $260\,^\circ\text{C}$ only afforded ethylbenzene, styrene, and guaiacol in yields of 7.1, 11.4, and 6.9%, respectively (Table 1, entry 7). In the reactions performed at low temperatures (Table 1, entries 2, 3, and 8) or without a catalyst (Table 1, entry 7), compound 1 underwent dihydroxylation, etherification, or demethoxylation to produce 1-methoxy-2-phenethoxybenzene, 1-methoxy-2-(2-methoxy-2-phenylethoxy)benzene, or 2-phenoxy-1-phenylethanol as the major byproduct. Notably, in all reactions, no cycloalkane product was detected, which suggests that W₂C holds promise as a substitute for noble metals in the hydrocracking of lignin β -O-4 bonds without destroying the aromatic rings. In contrast, hydrogenolysis of aryl ethers with noble metal catalysts typically produces a mixture of arenes, cycloalkanes, and phenols.^[16]



Scheme 1. C–O bonds cleavage of 2-(2-methoxyphenoxy)-1-phenylethanol catalyzed by W₂C/AC.

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Effects of solvent

The influence of solvent on the performance of chemical reactions is basically determined by the nature of the solvent and its dissolution ability. To realize a higher conversion for the reaction, several solvents such as THF, toluene, dioxane, and small-molecule alcohols, which were reported to solubilize lignin,^[16c,17] were screened for W₂C/AC-catalyzed β -O-4 cleavage. Importantly, THF, toluene, and dioxane are usually not preferred solvents for hydrogenation reactions, as they are liable to be destroyed. One of the advantages in this catalytic system is that the moderate catalytic activity of W₂C/AC and the low hydrogen pressure could leave these solvents untouched.

As shown in Table 2, although over 99% conversion was achieved in all cases by using the various solvents, under the identified conditions the product distribution was sensitive to the solvent selected. The results show that the yields of guaia-col (62.8–65.1%; Table 2, entries 1–3) were similar in the cases

Table 2. W_2C/AC -catalyzed hydrogenolysis of 2-(2-methoxyphenoxy)-1-phenylethanol in different solvents. ^[a]							
Entry	Solvent	Conv. [%]	Yield [%] ethylbenzene	styrene	E + S	guaiacol	
1 2 3 4 5 6 7 ^[b] 8 ^[c]	THF dioxane toluene H₂O ethanol methanol methanol methanol	100 99.5 100 100 100 99.8 100 34.8	15.6 4.1 37.2 0.8 39.2 88.4 13.5 3.1	35.0 31.2 21.7 1.0 22.0 8.5 71.1 25.0	50.6 35.3 58.9 1.8 61.2 96.8 84.6 28.1	62.8 65.1 64.7 51.8 75.5 93.0 98.7 29.7	
[a] Reaction conditions: unless otherwise specified, a stainless-steel auto- clave was charged with the substrate (100 mg), 30 wt% W ₂ C/AC (100 mg), and solvent (30 mL), and the reactions were conducted under an atmosphere of H ₂ (0.69 MPa) at 260 °C for 2 h. [b] The initial atmos- phere was argon (0.69 MPa) instead of H ₂ . [c] WO ₃ with an equal amount of tungsten was used as the catalyst; the reaction time was 2 h, and other conditions were the same as those outlined in entry 6.							

of THF, toluene, and dioxane; however, the yields of ethylbenzene and styrene were variously dependent on the nature of the solvent. Ethylbenzene was provided in lower yields in THF and dioxane (15.6 and 4.1%, respectively) than in toluene (37.2%), which implied that toluene was the preferred solvent for the styrene hydrogenation reaction. Nevertheless, severe side reactions occurred in the above three organic solvents, which resulted in the production of large amount of byproducts, including 2-phenylacetaldehyde, (E,Z)-(2-methoxyvinyl)benzene, 2-benzyl-1,3-dioxolane, 1-methoxy-2-phenethoxybenzene, and (E,Z)-1-methoxy-2-(styryloxy)benzene, as well as some unknown compounds (Figures S2-S4 in the Supporting Information), besides the target products. In chemical reactions, water is often chosen as a solvent because of its low cost, availability, and environmentally benignity, and we thus tested the reaction in water as the solvent. Unfortunately, this reaction only afforded trace amounts of ethylbenzene and styrene, as well as the lowest yield of guaiacol (Table 2, entry 4). As determined by GC with a flame-ionization detector (FID) and LC–UV results, no byproducts in the water reaction system were detected other than butane-1,3-diyldibenzene (2.7%, sty-rene dipolymerization product), 1-methoxy-2-phenethoxyben-zene (8.7%, dehydroxylation product of compound 1), and 2-phenoxy-1-phenylethanol (trace, methoxy group release product of compound 1). The poorest result can probably be attributed to the conversion of the initially formed intermediates, such as styrene, into insoluble products by polymerization.

It was interesting to find that small-molecule alcohols could significantly promote the conversion efficiency, which was evinced by a 75.5% yield of guaiacol, associated with a 61.2% total yield of ethylbenzene and styrene if ethanol was used as the solvent (Table 2, entry 5). Furthermore, the yield of guaiacol was increased to 93.0% and the total yield of ethylbenzene and styrene was up to 96.8% if methanol was employed (Table 2, entry 6). It was previously reported that Cu-doped porous metal oxides catalyzed the reforming of methanol above the supercritical temperature (239.6 °C) to produce hydrogen.^[18] Wang and Rinaldi also reported the hydrogen transfer of 2-propanol with Raney Ni for the upgrade of bio-oils.^[5d] We therefore envisaged the same scenario in our experiments. This speculation gained support from the following experiment. A control reaction with W₂C as the catalyst in methanol in the absence of the substrate was conducted at 260 °C for 2 h, and 0.69 MPa argon was used instead of H₂ as the initial atmosphere. After the reaction, the gases were captured and analyzed by GC with a thermal conductivity detector (TCD). It was interesting to find that besides the dominant argon component, minor components of H₂ and CO were detected (Figure S1), whereas these two gases were not formed in the absence of the catalyst. Thus, hydrogen must have originated from methanol by the reforming reaction as proposed in Ref. [18b]. The resulting hydrogen source provides the reducing equivalents necessary both to cleave the aromatic ethers and to reduce styrene further. This catalytic disassembly of compound 1 through hydrogen transfer from methanol was also confirmed by a reaction performed without any hydrogen gas (Table 2, entry 7). In this trial, 71.1% styrene was accompanied by 13.5% ethylbenzene (styrene hydrogenation product) and 98.7% guaiacol. Notably, styrene is much more valuable than ethylbenzene, as it is a precursor to many commercially significant products, including polystyrene, acrylonitrile butadiene styrene (ABS), styrene-butadiene rubber, styrenebutadiene latex, styrene-acrylonitrile resin, and unsaturated polyesters used in rubbers, plastics, insulation, and fiberglass.^[19] Styrene is mainly produced by the dehydrogenation of ethylbenzene in the presence of an iron oxide catalyst at high temperatures (600-650°C), but this process suffers from high energy consumption and a low yield of styrene owing to thermodynamic limitations of the endothermic reaction and deposition of dehydrogenated carbonaceous species.^[20] The above result provides a potential route to value-added styrene from lignin.

One of the advantages of using methanol as the solvent rather than ethanol is that cheaper methanol gives higher target product selectivity. Upon using ethanol as the solvent,



a considerable portion of byproducts, such as *n*-butylbenzene, 1-ethoxyethylbenzene, 2-ethoxyethylbenzene, 2-ethoxyphenol, 1-ethoxy-3-butenylbenzene, 2-phenylethanol, as well as 4-phenyl-2-butanol, were formed on the basis of GC–MS measurements (Figure S5). These compounds might be generated from the reactions of ethanol with intermediates/products by esterification and/or alkylation.

Conversion of various lignin β -O-4 model compounds

A series of 2-aryloxy-1-arylethanols with different substituents in the R¹, R², and R³ positions were employed as substrates (Table 3) for cleavage of β -O-4 bonds catalyzed by W₂C/AC under the same conditions as those outlined in entry 4 of Table 1. All these substrates (Table 3) have similar chemical groups and are found in different natural lignins.^[3] For example, 2-(2-methoxyphenoxy)-1-phenylethanol (substrate **1** in

Table 3. W ₂ '	C/AC-catalyz	w ₂ C/AC 0.69 MPa H ₂ , M	ond cleavage $\overrightarrow{R}^{(0)}$	$ \begin{array}{c} $	us 2-arylox	xy-1-aryeth + ^{R3}	OH C
Substrate	R ¹	R ²	R³	Conv. [%]	Yield [% A	6] B	с
1	Н	OCH₃	Н	99.8	88.4	8.5	93.0
2	Н	Н	Н	100	44.1	15.3	70.7
3	н	OCH ₃	OCH ₃	100	65.2	17.8	54.1
4	OCH₃	Н	Н	100	56.5	0	86.2
5	OCH ₃	OCH ₃	Н	100	71.5	0	78.0
6	OCH ₃	OCH ₃	OCH_3	100	82.8	0	48.4
[a] Reaction	conditions:	a stainless	-steel auto	clave was o	harged w	ith the su	ubstrate

(100 mg), 30 wt% W_2C/AC (100 mg), and methanol (30 mL); the reactions were conducted under an atmosphere of H_2 (0.69 MPa) at 260 $^\circ C$ for 2 h.

Table 3) is a major β -O-4 moiety in hardwoods such as birch.^[21] 2-Phenoxy-1-phenylethanol (substrate 2) without methoxy substitution on the phenyl ring is one component of grass lignin.^[22] After reaction, it was found that ethylbenzene and phenol derivatives (compounds A and C in Table 3) were the dominant products in all cases, which suggested that, in the W_2C /methanol system, the aryl C–O bonds of the substrates were selectively cleaved and the aryl rings were left intact in the products. The conversions of all substrates were higher than 99% in our reaction system; however, the yields of the aromatics varied (Table 2). Product B was not detected for the lignin model compounds with a methoxy group in the R¹ position (i.e., substrates 4-6), whereas those without a methoxy group in the R¹ position (i.e., substrates 1-3) afforded B in yields of 8.5 to 17.8%, which suggested that a methoxy group in the R¹ position accelerated the hydrogenation of the alkene in the para position. Electronic effects may have played an important role in this phenomenon, because product **B** with an electron-donating methoxy group favored adsorption of the catalyst. However, methoxy groups in the R² and R³ positions showed some diversity in hydrogenolysis behavior, which did not have a straightforward orderliness. Although we have no clear explanation for the results, they might arise from a combination of stereochemical and electronic effects. The methoxy groups in the R² and R³ positions (i.e., substrates **3** and **6**) provided the lowest yields of product **C** (2,6-dimethoxylphenol), whereas 3-methoxybenzene-1,2-diol and other byproducts derived from 2,6-dimethoxylphenol were detected, which implied that this compound was unstable in our catalytic system. Taking the results all together, W₂C/AC in methanol showed excellent activity in the cleavage of various β -O-4 linkages.

Catalyst stability and β-O-4 cleavage pathway

Catalyst reusability is one of the key factors affecting the potential use of a catalytic process. Therefore, W_2C/AC was recycled over five runs in the conversion of model compound 1 to test its stability. It can be seen in Figure 1 that the conversion

> over the catalyst was maintained at 100% even in the fifth run, and in parallel, the total yields of ethylbenzene plus styrene remained nearly constant over the five runs (from 89.9% to 86.5%), which suggested that the activity for cleavage of β -O-4 linkages was basically maintained, although the yield of guaiacol exhibited a slight decrease owing to demethoxylation and etherification side reactions, as trace amounts of phenol and 1,2-dimethoxybenzene appeared in the recycling runs. This result differs from that outlined in our previous report for the Ni-W₂C/ AC catalyzed processing of cellulose in water solven $t.^{\scriptscriptstyle [14a,23]}$ In that study, the catalyst was quickly deactivated in repeated runs owing to leaching of active species and oxidation of the W2C phase. It is interesting to point out that the W loadings of the fresh catalyst and the five-run catalyst were 30.2 and 27.0 wt%, respectively, according to inductively coupled plasma (ICP) analysis. This observation indicated

that leaching of the tungsten species was negligible in the methanol system, which might be an important reason for the good reusability of the catalyst for cleavage of β -O-4 linkages.



Figure 1. Recycling results for the W_2C/AC -catalyzed C–O bond cleavage of 2-(2-methoxyphenoxy)-1-phenylethanol. E+S is the abbreviation of the total yield of ethylbenzene plus styrene.

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Scheme 2. Proposed reaction pathway for the W₂C/AC-catalyzed deconstruction of 2-(2-methoxyphenoxy)-1-phenylethanol in alcohol solvent.

It was also found that the hydrogenation activity of the catalyst gradually decreased in the recycling runs according to the change in the yields of ethylbenzene (from 81.3% in the first run to 28.3% in the fifth run) and styrene (from 8.5% in the first run to 58.2% in the fifth run). Considering that styrene has higher value than ethylbenzene, a greater amount of styrene obtained in the recycling runs is beneficial for the production of value-added chemicals from lignin. X-ray diffraction (XRD) examinations demonstrated that the active W₂C phase on the after-run catalyst was slightly oxidized (shown in Figure S6). The Raman spectra of the catalysts also confirmed this observation (see Figure S7 for the Raman spectra and discussion). Transmission electron microscopy (TEM) images shown in Figure S8 indicate that large W₂C particles (10-20 nm) were formed on the AC supports for the fresh catalyst, whereas after it was used over five runs, W₂C nanoparticles were gradually transformed into WO_x nanofibers (10 nm width and 100 nm long), which is consistent with the XRD and Raman spectroscopy results. We therefore envisage that the increased yield of styrene can be attributed to partial oxidation of W₂C, which restrains the hydrogenation ability of the catalyst. Comparison experiments performed with the use of WO_3 and W_2C as the catalysts for the hydrogenation of styrene confirmed this speculation. Under the reaction conditions of Table 3, W₂C afforded a much higher yield (72.4%) of ethylbenzene than WO₃ (18.0%). Furthermore, the reaction of model compound 1 by using WO_3 (tungsten amount equal to that in W_2C/AC) in place of W₂C/AC provided a much lower conversion of 34.8%, and the yields of ethylbenzene, styrene, and guaiacol were 3.1, 25.0, and 29.7%, respectively (Table 2, entry 8 vs. 6). These results indicate that W_2C plays a key role in cleavage of the β -O-4 linkage in model compound 1.

To explore the principal conversion route of β -O-4 cleavage, we reanalyzed the liquid products of the low-temperature experiment in Table 1, entry 1. Besides the listed target products and two byproducts, 2-phenoxy-1-phenylethanol and 1-me-

thoxy-2-phenethoxybenzene, it was found that (E)- and (Z)-1methoxy-2-(styryloxy)benzene appeared in the GC-MS spectrum (Figure S9), whereas these two compounds could not be detected at higher reaction temperatures; this implies that they are active intermediates that readily undergo subsequent hydrogenolysis to styrene and guaiacol. Taking into account all intermediates and products formed in the above reactions (Figures S5 and S9), the overall reaction pathway for the W₂Ccatalyzed conversion of β -O-4 model compound 1 is proposed in Scheme 2. It proceeds by initial dehydration of compound 1 to form intermediate 7 (including the E and Z isomers), which is followed by hydrogenolysis of 7 to produce styrene and guaiacol and the hydrogenation of styrene to obtain ethylbenzene. Hydrogenolysis of 7 is proposed as the major route to the target products, because styrene and guaiacol are the dominant products at 200 °C (Table 1, entry 1). Hydrogenation of 7 to 8 followed by hydrogenolysis of 8 to ethylbenzene and guaiacol is a possible minor route, as compound 8 was detected. Moreover, compound 8 can produce 2-phenylethanol by hydrolysis according to Figure S5. Reaction of compound 8 provides evidence for the proposed reaction pathway. Under the conditions of Table 1, entry 4, compound 8 gives ethylbenzene (3.0%), guaiacol (4.9%), and 2-phenylethanol (trace) as the products with a conversion of 7.1%. Hydrolysis of 7 can generate guaiacol and 9, which tends to isomerize into 19. Further, direct hydrogenolysis of compound 1 occurs to produce guaiacol and 1-phenylethanol, and the latter is then etherified to 17 (Table S1). Other side reactions for the mechanism include polymerization of styrene to 11 and the demethoxylation, hydrogenolysis, and etherification of compound 1 to give 12, 13, and 14, respectively.

Conversion of realistic lignin feedstocks

The excellent results obtained with the model compounds motivated us to investigate the conversion of realistic lignin feed-



Table 4. Quantified liquid components obtained from the W ₂ C/AC-catalyzed valorization of BWL and CSL. ^[a]						
Monomer produced	Unit type	Yield [wt %] BWL	CSL	Select. ^[b] [wt %] BWL	CSL	
guaiacylpropanol	G	0.46	0	11.5	0	
guaiacylethanol	G	0.68	0.24	17.1	2.6	
syringylpropane	Sy	0.92	1.08	23.1	12.1	
syringylpropene	Sy	0.77	0.45	19.3	5.0	
guaiacylethane	G	0.11	0.39	5.3	4.3	
3,5-dimethoxy-4-hydroxyphenyl ethanone	Sy	0.22	0	2.7	0	
guaiacylpropane	G	trace	0.68	trace	7.6	
2,6-dimethoxyphenol	Sy	trace	0.71	trace	7.9	
2,6-dimethoxy-4-methylphenol	Sy	trace	0	trace	0	
1,2,3-trimethoxy-5-methylbenzene	Sy	trace	0	trace	0	
4-ethylphenol	Н	0.06	0.41	1.4	4.5	
4-methylphenol	Н	0	0.17	0	1.8	
benzene analogues	-	trace	0	trace	0	
fatty acid methyl esters	wax	0.41	0.05	10.30	0.6	
methyl hydrocinnamate	<i>p</i> -coumarate	0.37	1.57	9.2	17.5	
methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate	ferulate	0	0.87	0	9.6	
methyl 3-(4-hydroxy-3-methoxyphenyl)propanoic acid	ferulate	0	2.40	0	26.8	
total monomers		3.98	8.96			
oil yield		53.0	70.7			
monomers in oil		7.5	12.7			
[2] Position condition: a stainloss staal autoclave (Part 100 ml) was charged with lightin (200 mg) catalyst (200 mg) and mothanol (60 ml) with an initial						

[a] Reaction condition: a stainless-steel autoclave (Parr, 100 mL) was charged with lignin (200 mg), catalyst (200 mg), and methanol (60 mL) with an initial H₂ pressure of 0.69 MPa and reacting at 260 °C for 2 h. [b] Selectivity in total monomers.

stocks. One typical grass lignin extracted from corn stalk by the alkaline twin-screw extrusion process (denoted CSL in Table 4) and one typical wood lignin extracted from birch wood by the organosolv process (denoted BWL in Table 4) were selected as substrates to be depolymerized by the $W_2C/$ AC catalyst. Table 4 illustrates the yields of the phenolic oils and the monomer components of the oils. Interestingly, these two lignins were effectively converted into liquid oil in high yields of 70.7 and 53.0 wt%, respectively. The short growth period of corn stalk produces lignin with a looser structure [Figure S10, scanning electron microscopy (SEM) images] and a lower molecular weight [Table 5, gel-permeation chromatography (GPC) results] than birch wood lignin, and these are im-

Table 5. GPC results of BWL and CSL before and after reaction.					
Lignin sample	M _w	M _n	$M_{\rm w}/M_{\rm n}$		
fresh BWL	2757	920	3.00		
fresh CSL	1680	740 740	2.27		
CSL residue	715	191	3.70		

portant reasons why the oil yield from CSL is higher than that from BWL. Furthermore, the difference in the oil yield is probably due to the fact that each lignin resource has inherent variability in the chemical composition and pretreating may often make it even more complex. BET analysis of these two lignins showed that CSL had a larger surface area ($20.3 \text{ m}^2 \text{g}^{-1}$) than BWL ($11.1 \text{ m}^2 \text{g}^{-1}$), which is also in agreement with the conversion results.

Regarding the monomer composition, BWL yielded a broad variety of phenolic compounds, including guaiacylpropanol (11.5 wt% of the monomers), guaiacylethanol (17.1 wt%), syringylpropane (23.1 wt%), and syringylpropene (19.3 wt%) as the main products, which are derived from lignin guaiacyl (G) and syringyl (Sy) units. Other G and Sy monomers include guaiacylethane (5.3 wt%), 3,5-dimethoxy-4-hydroxyphenyl ethanone (2.7 wt%), and guaiacylpropane (trace). 2,6-Dimethoxyphenol, 2,6-dimethoxy-4-methylphenol, and 1,2,3-trimethoxy-5-methylbenzene are also derived from Sy-type precursors. In addition, a small amount of the p-hydroxyphenyl (H) unit 4-ethylphenol (1.4 wt% of the monomers) was detected in the liquid oil. Typically, hardwood lignin belongs to type G-Sy lignin, which comprises a mixture of Sy and G units along with a trace amount of the H unit. The BWL conversion results are in good agreement with the composition of hardwood lignin. For the liquid oil of CSL, the monomer composition is much different and more complicated than that of BWL. First, more H units (4.5 wt% 4-ethylphenol and 1.8 wt% 4-methylphenol) are comprised in the monomers, which leads to a Sy/G/H molar ratio of 42:36:22. It is known that corn stalk lignin is type H-G-Sy lignin with Sy, G, and H contents of 25-50, 25-50, and 10-25%, respectively.^[2a] Our result for the Sy/G/H molar ratio fits well with the literature. Second, in comparison with less noncanonical subunits contained in birch wood lignin, a much higher content of the p-coumarate unit methyl hydrocinnamate (17.5 wt% of monomers) along with trace amounts of fatty acid methyl esters were found in corn stalk lignin products. In addition, a dramatically higher amount of two ferulatederived units, methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate (9.6 wt%) and methyl 3-(4-hydroxy-3-methoxyphenyl)propanoic acid (26.8 wt%), were detected, which are in agree-



ment with the characterization results of Ralph and co-workers.^[24] These results suggest that corn stalk lignin contains a higher amount of noncanonical subunits than birch wood lignin.

The total percentage of monomers in the oil (7.5 wt% for BWL, 12.7 wt% for CSL; see Table 4) suggests that there are more products in the oil that could not be detected by GC–MS, a technique that can only detect compounds with low boiling points. To analyze the oil composition in more detail, orbitrap mass spectrometry was performed. Figure 2 shows the total ion current (TIC) traces of the BWL and CSL oil products. The obtained products from BWL are exclusively in the m/z=0-600 range, and no signal is detected after m/z=600 (Figure 2, top). Considering that typical Sy, G, and H units, for instance, syringylpropane, guaiacylethanol, and 4-propylphenol, have molecular weights of 168, 210, and 136 gmol⁻¹, respectively, it can be concluded that the obtained products from BWL include monomers, dimers, trimers, and tetramers with the first three as the main products. Regarding corn stalk

lignin, Figure 2 (botom) shows that the molecular weight distribution of the oil is much different from that of birch wood lignin. Not only were plenty of signals below m/z = 600 detected, but more interestingly, an abundance of higher molecular weight compounds appeared in the m/z = 600-1100 range, which implies that the CSL product distribution is much more complicated. This result is reasonable taking into account that corn stalk lignin contains more H units and noncanonical subunits than birch wood lignin.

Table 5 shows the GPC number average molecular weight (M_n) , weight average molecular weight (M_w) , and polydispersity (M_n/M_w) results of the fresh and residue lignins (relative to polystyrene standards). The residual lignin molecular weight decreased in both cases relative to that of the corresponding untreated lignins, which proved that depolymerization had occurred. Riedl et al. and Chakar and Ragauskas reported that during the degradation process, repolymerization (condensation) of lignin with active intermediates such as quinone methide and other radical phenolic species generated modified



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Figure 2. MS (ESI +) spectra of BWL liquid oil (top) and CSL liquid oil (bottom) (LTQ Orbitrap Elite, $m/\Delta m_{50} = 60\,000$ at m/z = 400).

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structures with higher molecular weights than the initial compounds.^[22,25] The decreased molecular weight of residue lignin in our case suggests that W_2C would not induce a severe repolymerization reaction, which is one of the advantages of this catalytic system.

To estimate the structural change of lignin before and after reaction, and to better understand the mechanism of C–O bond cleavage, fresh organsolv birch lignin (BWL) and the residue after the reaction were characterized by 2D-HSQC-NMR spectroscopy.

As shown in Figure 3 (top, left), cross-signals from the syringyl units are observed as prominent signals for the C_{2,6}–H_{2,6} correlation at approximately $\delta_C/\delta_H = 103.3/6.6$ and 105.3/ 7.3 ppm, whereas the guaiacyl unit correlations for C₂–H₂ are detected at $\delta_C/\delta_H = 110.7/7.3$ ppm, for C₅–H₅ at $\delta_C/\delta_H = 114.9/$ 6.8 ppm, and for C₆–H₆ at $\delta_C/\delta_H = 118.6/6.8$ ppm. Interestingly, signals related to the Sy units are more intense than those associated with the guaiacyl units, and the ratio of Sy/G is approximately 4.9. In the side-chain region, different signals can also be observed in the birch lignin. For example, in Figure 3



Figure 3. 2D-HSQC-NMR spectra of organosolv birch lignin in [D₆]DMSO/[D₅]pyridine (4:1 v/v) before the reaction (top, left and right) and the resulting residue mixture after treatment with our catalytic system (bottom, left and right).

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(top, right), BWL has a very high content of β -O-4 aryl ether linkages [up to 64.6% for A (β -O-4) and 16.5% for A' (β -O-4'), which is produced from pretreatment under acidic conditions with ethanol]^[26] with 0.7% resinol (B: β -5) and 18.2% phenylcoumaran (C: β - β). We also find from Figure 3 (top, right) that A is the dominant linkage in birch wood lignin, and the C_{α} -H_{α}, $C_{B}-H_{B}$, and $C_{v}-H_{v}$ correlations are observed at $\delta_{c}/\delta_{H}=72.0/5.0$, 86/4.2, and 60/3.5 ppm, respectively. In addition, a small amount of B is observed in Figure 3 (top, right) with C_{α} -H_{α}, C_{β} -H_{β}, and C_{γ} -H_{γ} correlations at δ_{C}/δ_{H} =87.1/5.5, 52.8/3.5, and 62.6/3.8 ppm, respectively, whereas signals from C are observed with C_{α} -H $_{\alpha}$ C_{β} -H $_{\beta}$, and double C_{γ} -H $_{\gamma}$ correlations at $\delta_{\rm C}/\delta_{\rm H}\!=\!85.0/4.7,\;53.6/3.1,\;71.0/3.8,$ and 71.0/4.2 ppm, respectively. After the reaction, the disappearance of the A, B, and C linkages of the residue is quite noticeable (Figure 3; bottom, left), which indicates these three linkages of A (β -O-4), B (α -O-4), and C (β - β) are attacked by the W₂C/AC catalyst, and cleavage of the C–O bond of β -O-4 is the major contribution. Interestingly, several cross-peaks at $\delta_{\rm C}/\delta_{\rm H} = 124 - 131/6.9 - 7.8$ ppm arise in the residue (Figure 3; bottom, right), probably owing to side reactions and the recombination of highly reactive radical intermediates. Additionally, after the reaction, the area of Sy and G in the lignin residue spectrum is significantly decreased (Figure 3 bottom, right vs. Figure 3 top, left), which suggests that most of the Sy and G aromatic structures are converted or released in the oil products. This above result is in good agreement with the orbitrap mass spectrometry and GPC results.

On the basis of the conversion results and HSQC analysis, one can conclude that W₂C/AC shows high activity not only in β -O-4 cleavage but also in the cleavage of the more resistant α -O-4 and β - β linkages for lignin conversion, so as to obtain a high yield of liquid oil products. Notably, no cycloalkane was detected in the two liquid oils, which further confirms that W₂C/AC is highly selective in the cleavage of aryl C–O bonds in lignin.

For a catalytic process, a high substrate concentration is expected to be valuable in facilitating the cost-efficient conversion of biomass into biobased products. We tested the conversion of CSL with a higher concentration (3 g lignin in 60 mL methanol), and an oil yield of 42.0 wt% was obtained (for details, see Table S3). Despite the fact that this result is lower than that obtained with a lower concentration of realistic lignin, it is fairly good taking into account the much higher substrate concentration. It should be noted that although several methods^[27] have been developed for the fractionation of phenolic compounds from a lignin depolymerization mixture, because of the complicated composition of the oil and the similar properties of the phenolic products, it is still a big challenge to isolate target chemicals selectively from the reaction mixture.

Conclusions

In summary, by using the cheap W_2C /activated carbon (AC) catalyst, it was possible to convert various lignin model compounds and realistic lignin materials selectively into monophe-

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nols and liquid oils in high yields. W₂C/AC exhibited promising potential for the substitution of noble metals in the cleavage of the major aryl ether bonds of lignins without destroying the aromatic rings. Methanol was the preferred solvent because W₂C/AC catalyzed the in situ hydrogen-transfer reaction from methanol to the substrate. W₂C/AC exhibited high activity not only in β-O-4 cleavage but also in the deconstruction of more resistant α-O-4 and β-β linkages in lignin. More importantly, this catalyst could be reused five times without a significant loss in C–O bond-cleavage activity. These features make this simple catalytic process highly effective and environmentally green. Furthermore, the high yield of the aromatic bio-oil obtained from lignin without the formation of cycloalkanes is of great significance for the cost-efficient production of aromatic chemicals from biomass.

Experimental Section

Materials and analysis methods

WO₃ was purchased from Aladdin Chemistry Co., Ltd., Shanghai, China. All lignin model compounds, β -hydroxy ether substrates,^[28] and the W₂C/AC catalyst^[14a] were prepared as described in our previous paper. Elemental analysis of the leached (or dissolved) catalyst was accomplished by using a Thermo iCAP Model 6300 inductively coupled plasma atomic emission spectrometer (ICP-AES). Xray diffraction (XRD) patterns of the catalysts were recorded with a PW3040/60 X'Pert PRO (PANalytical) diffractometer equipped with a CuK_{α} radiation source ($\lambda = 0.15432$ nm). The Raman spectra were recorded with a Horiba Jobin Yvon T64000 system (Horiba, Japan) equipped with a confocal microscope. The molecular weights of the lignin and residues were analyzed with a gel-permeation chromatograph (Viscotek TDAmax). NMR spectra were recorded with a Bruker Avance DPX-400 spectrometer at 298 K. Detailed synthesis procedures and characterization methods as well as supporting figures are provided in the Supporting Information.

Typical procedure for C–O cleavage of lignin model compounds

The catalytic conversion of lignin model compound was performed in a stainless-steel autoclave (Parr, 100 mL) with an initial H₂ pressure of 0.69 MPa. Typically, the stainless-steel autoclave was charged with the lignin model compound (100 mg), catalyst (100 mg), and methanol (30 mL), and the autoclave was then charged with an initial H₂ pressure of 0.69 MPa; the mixture was stirred (800 rpm) at 260 °C for 2 h. After the reaction, the mixture was cooled to room temperature and filtered. The liquid phase was analyzed by GC-FID and was quantified by the internal standard method (standard: mesitylene, HP-5 column, 30 m × 0.32 mm × 0.25 μ m).

Typical procedure for the W₂C/AC-catalyzed depolymerization of lignin feedstocks

The catalytic conversion of lignin material was performed in a stainless-steel autoclave (Parr, 100 mL) with an initial H_2 pressure of 0.69 MPa and 260 °C for 2 h. Typically, the autoclave was charged with lignin (200 mg), catalyst (200 mg), and methanol (60 mL), and the mixture was stirred at a rate of 800 rpm. After the reaction, the mixture was cooled to room temperature and filtered. The solid



residue was washed with methanol and dried at 50 °C under vacuum for 2D-HSQC-NMR characterization. The filtrate was concentrated under reduced pressure at 35 °C to obtain the liquid oil, which was weighed. The liquid oil was then diluted to 2 mL with methanol, and the monomer products in the liquid oil were analyzed and quantified by the internal standard method (standard: mesitylene) with an HP 5973 GC-MS (HP-5 column, 30 m× 0.32 mm×0.25 µm). The molecular weight distribution of the liquid oil was analyzed by orbitrap mass spectrometry in the mass range of m/z=50 to 2000 (LTQ Orbitrap Elite, positive-ion ESI-MS, $m/\Delta m_{s0}=60000$ at m/z=400).

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- a) M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* 2014, *114*, 1827–1870;
 b) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 2007, *107*, 2411–2502; c) J. A. Melero, J. Iglesias, A. Garcia, *Energy Environ. Sci.* 2012, *5*, 7393–7420.
- [2] a) C. Li, X. Zhao, A. Wang, G. W. Huber, T. Zhang, *Chem. Rev.* 2015, *115*, 11559–11624; b) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* 2010, *110*, 3552–3599.
- [3] L. H. Hu, H. Pan, Y. H. Zhou, M. Zhang, Bioresources 2011, 6, 3515-3525.
- [4] a) C. A. Gasser, G. Hommes, A. Schäffer, P. F. X. Corvini, Appl. Microbiol. Biotechnol. 2012, 95, 1115 – 1134; b) J. E. Holladay, J. F. White, J. J. Bozell, D. Johnson, Top Value-Added Chemicals from Biomass, Vol. II, Results of Screening for Potential Candidates from Biorefinery Lignin, U.S. Department of Commerce, Virginia, 2007.
- [5] a) C. P. Xu, R. A. D. Arancon, J. Labidi, R. Luque, *Chem. Soc. Rev.* 2014, *43*, 7485–7500; b) A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan, C. E. Wyman, *Science* 2014, *344*, 1246843; c) R. G. Harms, I. I. E. Markovits, M. Drees, W. A. Herrmann, M. Cokoja, F. E. Kühn, *ChemSusChem* 2014, *7*, 429–434; d) X. Y. Wang, R. Rinaldi, *Angew. Chem. Int. Ed.* 2013, *52*, 11499–11503; *Angew. Chem.* 2013, *125*, 11713–11717; e) X. Y. Wang, R. Rinaldi, *ChemSuschem* 2012, *5*, 1455–1466; f) P. Ferrini, R. Rinaldi, *Angew. Chem. Int. Ed.* 2014, *53*, 8634–8639; *Angew. Chem.* 2014, *126*, 8778–8783.
- [6] A. Toledano, L. Serrano, A. Pineda, A. A. Romero, R. Luque, J. Labidi, *Appl. Catal. B* 2014, 145, 43–55.
- [7] C. Zhao, J. A. Lercher, ChemCatChem 2012, 4, 64-68.
- [8] N. Yan, Y. Yuan, R. Dykeman, Y. Kou, P. J. Dyson, Angew. Chem. Int. Ed. 2010, 49, 5549-5553; Angew. Chem. 2010, 122, 5681-5685.
- [9] N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. Liu, Y. Kou, *ChemSusChem* 2008, 1, 626-629.

[10] J. G. Zhang, H. Asakura, J. van Rijn, J. Yang, P. Duchesne, B. Zhang, X. Chen, P. Zhang, M. Saeys, N. Yan, *Green Chem.* 2014, *16*, 2432–2437.

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- [11] B. Feng, H. Kobayashi, H. Ohta, A. Fukuoka, J. Mol. Catal. A 2014, 388, 41–46.
- [12] H. Konnerth, J. G. Zhang, D. Ma, M. H. G. Prechtl, N. Yan, Chem. Eng. Sci. 2015, 123, 155–163.
- [13] a) R. J. Hou, K. Chang, J. G. G. Chen, T. F. Wang, *Top. Catal.* 2015, *58*, 240–246; b) E. F. Mai, M. A. Machado, T. E. Davies, J. A. Lopez-Sanchez, V. T. da Silva, *Green Chem.* 2014, *16*, 4092–4097; c) H. Shou, R. J. Davis, *J. Catal.* 2013, *306*, 91–99; d) M. L. Frauwallner, F. Lopez-Linares, J. Lara-Romero, C. E. Scott, V. Ali, E. Hernandez, P. Pereira-Almao, *Appl. Catal. A* 2011, *394*, 62–70; e) R. Ma, W. Y. Hao, X. L. Ma, Y. Tian, Y. D. Li, *Angew. Chem. Int. Ed.* 2014, *53*, 7310–7315; *Angew. Chem.* 2014, *126*, 7438–7443; f) A. L. Jongerius, R. W. Gosselink, J. Dijkstra, J. H. Bitter, P. C. A. Bruijnincx, B. M. Weckhuysen, *ChemCatChem* 2013, *5*, 2964–2972.
- [14] a) N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J. Chen, Angew. Chem. Int. Ed. 2008, 47, 8510–8513; Angew. Chem. 2008, 120, 8638–8641; b) A. Q. Wang, T. Zhang, Acc. Chem. Res. 2013, 46, 1377– 1386.
- [15] C. Z. Li, M. Y. Zheng, A. Q. Wang, T. Zhang, *Energy Environ. Sci.* 2012, 5, 6383–6390.
- [16] a) W. Zhang, J. Z. Chen, R. L. Liu, S. P. Wang, L. M. Chen, K. G. Li, ACS Sustainable Chem. Eng. 2014, 2, 683–691; b) J. He, C. Zhao, D. Mei, J. A. Lercher, J. Catal. 2014, 309, 280–290; c) Q. Song, F. Wang, J. Xu, Chem. Commun. 2012, 48, 7019–7021.
- [17] a) J. S. Luterbacher, A. Azarpira, A. H. Motagamwala, F. C. Lu, J. Ralph, J. A. Dumesic, *Energy Environ. Sci.* **2015**, *8*, 2657–2663.
- [18] a) T. D. Matson, K. Barta, A. V. Iretskii, P. C. Ford, *J. Am. Chem. Soc.* 2011, *133*, 14090–14097; b) G. S. Macala, T. D. Matson, C. L. Johnson, R. S. Lewis, A. V. Iretskii, P. C. Ford, *ChemSuschem* 2009, *2*, 215–217.
- [19] N. Jiang, A. Burri, S.-E. Park, Chin. J. Catal. 2016, 37, 3-15.
- [20] L. Zhang, Z. L. Wu, N. C. Nelson, A. D. Sadow, I. I. Slowing, S. H. Overbury, ACS Catal. 2015, 5, 6426–6435.
- [21] K. Gabov, R. J. A. Gosselink, A. I. Smeds, P. Fardim, J. Agric. Food Chem. 2014, 62, 10759–10767.
- [22] H. Nadji, Y. Bedard, A. Benaboura, D. Rodrigue, T. Stevanovic, B. Riedl, J. Appl. Polym. Sci. 2010, 115, 1546–1554.
- [23] N. Ji, T. Zhang, M. Y. Zheng, A. Q. Wang, H. Wang, X. D. Wang, Y. Y. Shu, A. L. Stottlemyer, J. G. G. Chen, *Catal. Today* **2009**, *147*, 77–85.
- [24] S. D. Mansfield, H. Kim, F. C. Lu, J. Ralph, *Nat. Protoc.* 2012, *7*, 1579–1589.
- [25] F. S. Chakar, A. J. Ragauskas, Ind. Crops Prod. 2004, 20, 131-141.
- [26] J. M. W. Chan, S. Bauer, H. Sorek, S. Sreekumar, K. Wang, F. D. Toste, ACS Catal. 2013, 3, 1369–1377.
- [27] a) K. Barta, T. D. Matson, M. L. Fettig, S. L. Scott, A. V. Iretskii, P. C. Ford, *Green Chem.* 2010, *12*, 1640–1647; b) V. M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. B. Li, J. A. Lercher, *Chem. Eur. J.* 2011, *17*, 5939–5948; c) J. H. P. M. Santos, M. Martins, A. J. D. Silvestre, J. A. P. Coutinho, S. P. M. Ventura, *Green Chem.* 2016, *18*, 5569–5579.
- [28] B. Zhang, C. Z. Li, T. Dai, G. W. Huber, A. Q. Wang, T. Zhang, RSC Adv. 2015, 5, 84967–84973.

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Breaking up: Tungsten carbide shows remarkable activity in selective C–O bond cleavage of typical β -O-4 model compounds and deconstruction of lignin feedstocks. High yields of C–O cleavage products from model compounds (up to 96.8%) and from lignin feedstock (up to 70.7%) are obtained without destroying the aromatic rings.



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Tungsten Carbide: A Remarkably Efficient Catalyst for the Selective Cleavage of Lignin C–O Bonds