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Selective C-C Bond Cleavage of Methylenelinked Lignin Models and Kraft Lignin

Li Shuai, Jake Sitison, Sunitha Sadula, Junhuan Ding, Mark Charles Thies, and Basudeb Saha ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.8b00200 • Publication Date (Web): 05 Jun 2018 Downloaded from http://pubs.acs.org on June 5, 2018

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Selective C–C Bond Cleavage of Methylene-linked Lignin Models and Kraft Lignin Li Shuai[¥], Jake Sitison[¥], Sunitha Sadula[¥], Junhuan Ding[§], Mark C. Thies[§], Basudeb Saha^{¥*} [¥]Catalysis Center for Energy Innovation, University of Delaware, 221 Academy Street, Newark, DE 19716, USA [§]Department of Chemical and Biomolecular Engineering. Clemson University 221 Earle Hall, Clemson, SC 29634, USA

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ABSTRACT

Biorefinery and paper pulping lignins, referred hereto as technical lignins, contain condensed C–C interunit linkages. These robust C–C linkages of higher bond dissociation energies are difficult to disrupt under hydrogenolysis condition, which is generally used for cleaving C–O bonds of native lignin in biomass or model C–O linked compounds. Thus, selective C–C bonds cleavage to release aromatic monomers for high value applications is a challenge. We report an effective catalytic system to cleave such C–C bonds selectively under mild conditions. A representative methylene-linked C-C model dimer achieves 88% yield of mainly two aromatic monomers within 1.5 h at reasonably low temperature (250 °C) using a commercial CoS₂ catalyst. Aromatic monomers convert to non-aromatic products upon reaction for a prolonged time. C–C bond of the dimer becomes unreactive to cleavage upon dehydroxylation of aromatic rings while the methoxyl group has a little effect to the cleavage. β -1 and 5-5 C-C linked model dimers formed demethoxylated hydroxyl dimers as the major products. Depolymerization of a purified kraft lignin fraction yields five aromatic monomers and lower molecular weight soluble products. This study opens up the possibility of valorization of technical lignin using inexpensive catalysts.

Keywords: Technical lignin, kraft lignin, C-C cleavage, model lignin, biorefinery lignin, selective catalysis.

INTRODUCTION

Technical lignins, generated by biorefinery and paper pulping industries, are considered as low value waste streams, and their valorization have intrigued researchers for decades.

Researchers have made numerous efforts to disrupt technical lignins into low molecular weight (Mw) fragments to upgrade to value-added aromatic products.^{1, 2} Recent efforts on lignin valorization have been mainly focused on selective cleavage of β -O-4 (β -ether) linkages, which represent the major interunit linkages (50-60%) in native lignin of lignocellulosic biomass,³⁻⁶ with the balance being α -O-4 and various C-C linkages, such as β -5, β -1 and 5-5.^{3, 7}



Scheme 1. Representative lignin structure featuring interunit C–O (e.g. β –O–4, highlighted in blue) and C–C (e.g. β – β , β –5 and 5–5, highlighted in red) linkages and current 'lignin-first' strategy to produce monomer in which C-C bonds are uncleavable.

Hydrolysis,⁸ hydrogenolysis,⁹⁻¹⁴ and oxidation^{15, 16} pathways have been widely investigated for lignin depolymerization (Scheme 1). Hydrogenolysis is a selective method to depolymerize lignin to monomers via β -O-4 bonds cleavage;^{4, 9-12} however, total monomer yield is limited by robust C-C interunit linkages.

In contrast, technical lignin contains mostly C–C bonds, which are formed during biomass pretreatment or pulping processing. Higher bond dissociation energies (BDEs) of C–C bonds (75–118 Kcal/mol) than that of C–O linkages (70 Kcal/mol) pose challenges to depolymerize technical lignins selectively under mild conditions (Scheme 1).^{17, 18} For example, hydrogenolysis depolymerzation of organosolv lignin achieved only 7% monomer yield,¹¹ while depolymerization of native lignin or uncondensed lignin yielded up to 48% monomer upon cleaving β –O–4 bonds.^{3, 19, 20} Similarly, hydrogenolysis depolymerization of kraft lignin with Pt/Al₂O₃ at 250–300 °C formed about 7% monomer yield.^{21, 22} Catalytic pyrolysis of alkali kraft lignins with strong solid acids or solid acid-supported catalysts at elevated temperatures (up to

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Another common issue of current processes is very low selectivity of each product, rendering any separation approach energy-intensive and expensive. For example, kraft lignin depolymerization in ethanol under pyrolysis condition (380 °C) produced over three dozen monomers, out of which total aromatic phenols was only 10%.²⁵ Efforts have been made to study the cleavage of model compounds featuring 5–5, β –5 and β –1 linkages, but the saturation or disruption of aromatic rings and C–O cleavage were observed, instead of C–C cleavage, under hydrogenolytic and oxidative conditions.^{26, 27} A CoMo/Al₂O₃ catalyst was found to be ineffective to cleave 5-5' linkage of a model dimer in a prior study²⁸ while a flower like hierarchical MoS₂ composite²⁹ offered unselective bio-oil yield at higher temperature (310 °C), likely via thermopyrolysis. Because of rigidity of C–C linkages and the structural complexity, majority of 80 million tons of technical lignins annually generated in pulping and biorefinery processes is considered as a low-value waste and burned only for heat recovery.³⁰

Efficient conversion technologies to depolymerize technical lignins into high-value fuels and aromatic products are necessary to maximize waste utilization and carbon efficiency in bioproducts, and to create additional revenue for pulping and biorefineries. Prior reports suggest that methylene linkages could be formed in technical lignins during self-condensation or in-situ generated formaldehyde-induced condensation of depolymerized lignin fragments containing aromatic rings with α -hydroxyl side chain functionality in acidic and alkaline media.^{25, 31-33} Herein, we report an effective approach to improve selective depolymerization of technical lignin using model lignin dimers (dimethylguaiacylmethane DMGM; Figure 1A and its dehydroxylated analogues) and purified kraft lignin as representative examples. First, we evaluate the activity of a few types of readily available metal sulfides to disrupt methylene linkage of DMGM. The synthesis of DMGM featuring a methylene linkage is shown in the supporting information (Figures S1-S3). The reasons to choose this type of catalysts are: (1) kraft lignin generally contains 1.5-3% of sulfur which comes from Na₂S, a chemical reagent promoting lignin removal during biomass pretreatment. Metal sulfides are expected to be resistant to sulfur poisoning, and (2) metal sulfides, such as FeS₂, CoS₂ and MoS₂, exist naturally in highly pure forms, therefore these inexpensive materials are economically suitable for upgrading waste lignin liquor.

RESULTS and DISCUSSION

FeS₂ has been used as a catalyst for hydrocracking of heavy oils containing aromatic units at 300-450 °C. These studies have found that FeS2 can cleave interunit C-C bridge linkages between aromatic rings.³⁴ Therefore, we first tested FeS₂ as the catalyst to disrupt the methylene linkage of DMGM at 250 °C and 50 bar H₂. Monomeric and a small amount of dimeric products are formed (Figures 1A and S4). Some of the resultant monomers having one or two isomers are grouped for simplification and their retention times are shown in Figure S4. Without FeS_{2} , DMGM depolymerization at 250 °C and 50 bar H₂ for 15 h achieves only 15% conversion (Figure S5) likely via thermal pyrolysis. Pyrolysis of lignin to monomers without catalysts and H₂ input has been reported previously.³⁵ In the presence of FeS₂, monomer yield of 64% with 97% selectivity is achieved under comparable reaction conditions. This temperature (250 °C) has been widely used in hydrogenolysis cleavage of β -O-4 linkages of native lignin or model lignin compounds with Ni/C, Ru/C and Pt/C catalysts,^{1, 4, 5, 11, 19, 36} which allows a fair comparison of the catalytic activity of the two types of catalysts for cleavage of the respective C-C and C-O bonds (vide infra). The reaction is ineffective at 200 °C, giving no conversion of DMGM in the presence of FeS₂. While the results with FeS₂ at 250 °C, giving 64% total monomer yield containing five phenolic products, is more selective than prior arts demonstrating formation of heterogeneous slates of molecules under pyrolysis conditions, the separation of desired monomer from the five products is still a challenge. In addition, 30% of demethoxylated and dehydroxylated dimeric products with partial ring-hydrogenation (Figures S4 and S5) are formed, which are proven to be uncleavable (vide infra). Therefore, we tested two other metal sulfides, MoS₂ and CoS₂.

The MoS₂-catalyzed reactions under comparable conditions as FeS₂ formed a little amount of monomer (8%) and a significant amount of demethoxylated and dehydroxylated dimers with or without partial ring hydrogenation (Figures S4 and S6), which remained uncleaved. In contrast, initial CoS₂-catalyzed reaction at 250 °C and 50 bar H₂ for 15 h produced only three monomers (B, D and E in Figure 1A and Figure S6). The clean dimer region in the GC chromatogram (retention time of 11.7–16.5 min in Figure S6) indicates the methylene linkage of DMGM was selectively cleaved without formation of uncleavable dimeric products. However, the initial reaction for 15 h gives only low yield of aromatic monomers. We hypothesize the low

yield could be due to the further conversion of aromatic monomers to other products during a long reaction time of 15 h. Therefore, a time-course experiment was conducted to study the reaction profile of the CoS_2 -catalyzed disruption of DMGM.

The time-course results show selective formation of two aromatic monomers B and C (Figure 1B) in the beginning of the reaction and total monomer yield reached to 88% within 1.5 h (Figures 1A and S7, Table S1). B and C convert to other two aromatic monomers, D and E (Figure 1A) through possible dehydroxylation and demethoxylation, when the reaction continued for 4 h. Complete and partial ring hydrogenated non-aromatics products, methyl cyclohexene and cyclohexane (Figures 1A and S7, Table S1) are formed upon continuing the reaction for 15 h. A small amount demthoxylated and dehydroxylated dimeric products are also formed. We



Figure 1. (A) Proposed pathways for metal sulfide-catalyzed methylene linkage disruption of dimethylguaiacylmethane (DMGM); (B) The time-course reaction profile for CoS_2 -catalyzed DMGM disruption, showing selective formation of aromatic monomer in short reaction time. Reaction conditions for the time-course experiments: 20 mg DMGM, 10 mg CoS_2 , 50 bar H₂, 250 °C, 20 mL heptane.

hypothesize that the dimers become uncleavable after losing the methoxyl and/or hydroxyl groups of DMGM. To validate the hypothesis, we investigate C–C cleavage of other model dimers containing a methylene linkage, but without methoxyl and/or hydroxyl groups (Figure S8). The results show the methylene linkage of a model dimer with a phenolic hydroxyl on both aromatic rings but without methoxyl can still be cleaved with 77% conversion in 1.5 h,

suggesting that the methoxyl group has a little effect on the cleavage of C–C bonds. Another model dimer with one phenolic hydroxyl group on one ring and no phenolic hydroxyl on the second ring results in low conversion (20%) under comparable reaction conditions. This indicates the cleavage of the methylene linkage depends on the chemical environments of lignin molecules, especially the vicinal phenolic groups which likely interact with Co²⁺ sites of cobalt-sulfide and strong electron-donating effect of the phenolic groups weaken the methylene linkage. This argument becomes more pronounced when an analogous diphenyl model compound without any phenolic hydroxyl group substituent showed no C–C cleavage. Likewise, β -1 and 5-5 linked model dimers formed their corresponding demethoxylated hydroxyl dimers as the major products (Figure S8).

To elucidate the transformation of monomers B and C to monomers D and E, B and C were reacted individually with the CoS_2 catalyst under comparable reaction conditions used for the disruption of model dimers. B converts to E through dehydroxylation, but demethoxylation of C formed B and E. A reaction with a mixture of B and C also gives E as the sole product. Based on the aforementioned discussion (Figures S7-S9), a proposed reaction pathway for the CoS_2 catalyzed DMGM disruption is shown in Figure 1, although the exact pathway of formation of D is inconclusive.

Next, we test the role of H_2 for cleavage of the methylene linkage of DMGM. At 10 bar H_2 , DMGM conversion achieved only 21% as opposed to nearly 90% at 50 bar H_2 (Table S2). Another experiment at 10 bar H_2 but total pressure of 50 bar using N_2 as an inert gas improved monomer yield slightly (27%) due to better H_2 solubility in the solvent. Without H_2 , DMGM is unreactive, indicating the C-C cleavage is likely H_2 -assisted as reported for C-O cleavage of lignin compounds.³⁷

We used Ru/C and Pt/C catalysts to compare their C-C cleavage performance with CoS₂. These noble metal catalysts have been used to selectively cleave β –O–4 linkages of model and native lignins via hydrogenolysis, but C–C cleavage of lignin by these catalysts is rare.^{26, 27, 38} The results in Table 1 show that CoS₂ exhibits much higher activity to cleave C-C linkage to two monomers (B and C) with 81% yield out of total molar yield of 88% (entry 1 in Table 1). In contrast, the Ru/C and Pt/C catalyzed reactions yield very little monomer (total yields of B and C are 9.9 % and 4.1%, respectively; entries 2 and 3 in Table 1), which likely result from small amount of thermo-pyrolysis at 250 °C as observed in the blank experiment without the catalyst

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(discussed above). The results reveal that CoS_2 is very effective and selective towards aromatic monomers with high yield at high conversion of DMGM in heptane.

 Table 1. Comparison of CoS₂- and noble metal catalyzed DMGM disruption

 and kraft lignin depolymerisation.^[a]

Entry	Feedstock	Solvents	Catalysts	Catalyst loading (mg)	Aromatic monomer yield (%)
1	DMGM	Heptane	CoS_2	10	88 ^[b]
2	DMGM	Heptane	Ru/C	10	9.9 ^[c]
3	DMGM	Heptane	Pt/C	10	4.1 ^[d]
4	Lignin ^e	Heptane	CoS_2	50	1.2
5	Lignin ^e	Dioxane	CoS_2	50	11.7
6	Lignin ^e	Dioxane	CoS_2	100	13.2
7	Lignin ^e	THF	CoS ₂	50	12.6

[a] Other reaction conditions: 50 bar H₂, 250 °C, 1.5 h for dimer or 15 h for kraft lignin, 50 mg kraft lignin or 20 mg DMGM. [b] dimer conversion 100%; [c] dimer conversion 15.3%; [d] dimer conversion 5%; [e] kraft lignin (alkali) fraction purified by ALPHA process.³⁹ Comparison of breakdown monomer yield from CoS₂, Ru/C and Pt/C catalysis of DMGM is in Table S3. Ru/C catalyzed kraft lignin depolymerized monomer yields in heptane and dioxane are shown in Table S4.

Next we evaluate depolymerization of a low Mw fraction of a kraft lignin of average Mw of 1600 Da and the highest Mw species ranged up to 10000 Da (Figure 2) with CoS₂. The kraft lignin fraction was obtained from purification and fractionation of an alkali kraft lignin via the Aqueous Lignin Purification with Hot Acids (ALPHA) process,³⁹ followed by a single water wash to remove the acetic acid solvent, reduce the total metals content to <200 ppm, and then drying to remove excess water. The ALPHA process had no effect on the original sulfur content of the kraft lignin. Depolymerization with Ru/C was also performed for comparison. Initial

results show poor depolymerization of the kraft lignin fraction in heptane (entry 4 in Table 1), which we ascribed to its low solubility in heptane. The solvent screening results suggest that the kraft lignin fraction has higher solubility in dioxane and tetrahydrofuran (THF). In dioxane, CoS_2 catalysis achieves maximum 13% monomer yield (entries 5-6 in Table 1). A reaction in THF yields similar amount of monomers (entry 7). In contrast, Ru/C-catalyzed reactions in heptane and dioxane at two different catalyst loadings (20 mg and 100 mg) yield maximum 5% aromatic monomers (Figure S10; Table S4), which are likely formed via cleavage of a small amount of β –O–4 linkages (5-7%²¹) present in the kraft lignin fraction. However, the structural complexity of the condensed kraft lignin makes it difficult to explain of which linkages (methylene versus other C–C bonds) were disrupted during the reaction. In addition, Mw species that are outside the detectable range of GC/GC-MS could be formed. Therefore, gel permeation chromatography (GPC) was used to qualitatively characterize the change in Mw of lignin species before and after depolymerization.

Figure 2 shows the highest Mw species in the kraft lignin fraction before depolymerization is ranged up to 10000 Da with an average Mw of about 1600 Da. In contrast, the average Mw of depolymerized lignin is decreased by about 3-5 folds and the Mw distribution range is significantly narrowed. The shape of the peak, Mw distribution range and average Mw of depolymerized lignin at two different Ru/C loadings are similar, indicating that increasing Ru/C loading could not further cleave interunit C–O or C–C linkages, consistent with similar monomer yields obtained from the two reactions, (Table S4). In case of CoS₂, Mw distribution range of depolymerized lignin is narrower than that of the Ru/C catalyzed depolymerization, indicating a greater degree of depolymerization of kraft lignin occurred. Furthermore, average Mw and the range of the highest Mw of the depolymerized species decreased with an increase in CoS₂ loadings, indicating C–C cleavage occurred by the CoS₂ catalyst, in addition to any C-O cleave of small amount of C-O linkages that are present in kraft lignin. This observation is also consistent with the results of DMGM cleavage in which monomer yield increased with CoS₂ loadings.



Figure 2. GPC of a kraft lignin fraction before and after depolymerisation with CoS_2 and Ru/C.

CoS₂ catalyzed reaction also generated H₂S (Figure S11), hypothesizing CoS₂ could be reduced to CoS by H₂ during the reaction. The XRD pattern of the recovered catalyst validates the hypothesis, which showed the characteristic peaks for CoS (Figure S12). In addition, CoS₂ was treated in heptane and dioxane individually in the absence and presence of H₂ without DMGM or lignin, and the recovered catalyst was characterized by the XRD. The recovered catalyst retained characteristic CoS₂ peaks in the absence of H₂, however it changed to CoS in the presence H₂ (Figure S13) in both the solvents. Thus, CoS₂ may not be the active phase for the C-C cleavage. A CoS, synthesized by the reported procedure,⁴⁰ yield 7.7% and 11.1% monomer from the kraft lignin fraction at the catalyst loading of 50 mg and 100 mg, respectively, which are slightly lower than that from the CoS₂-catalyzed reactions (entries 5 and 6 in Table1).

Recycling study of CoS_2 shows (Figure S14) the recovered catalyst is slightly less active and total monomer yield in the 3rd cycle is 14% lower than that in the 1st cycle. Compositional analyses of CoS_2 and the recovered catalyst by XRF (for Co and S) and elemental analyzer (for S) indicate the atomic ratio of Co to S in the catalyst before the reaction is 1: 1.7 while the ratio decreased to 1:1 in the recovered catalyst after the reaction. The compositional analysis data is consistent with the XRD pattern discussed above and suggests that the catalyst was reduced to CoS by H₂ during the reaction and. XPS was employed to examine the surface composition and oxidation states of Co and S of the catalysts before and after C-C cleavage of DMGM (Figure

S15). Deconvoluted Co $2p^{3/2}$ band shows peaks for CoS₂, CoS, Co(OH)₂ and CoO at binding energies (BE) of ~777.2 eV, 781.5 eV, 784.0 eV and 786.8 eV respectively, according to prior assignment.⁴¹⁻⁴³ The recovered catalyst shows an increased intensity ratio of CoS and a decreased ratio of CoS₂, which is consistent with the changing trend of S in the deconvoluted S 2p band. The S 2p band of the catalyst before reaction shows BE peaks for S²⁻ (monosulfide), S₂²⁻ (disulfide), S_n²⁻ (n > 2, polysulfides) and S⁰ (elemental S) at ~161.5 eV, 162.5 eV, 163.7 eV and 164.4 eV, respectively, according to prior assignment.⁴⁴ After reaction, the ratio of S²⁻ increased and the ratio of S₂²⁻ decreased, indicating the structural change of the catalyst to CoS occurred during the reaction. A controlled experiment using a commercial cobalt oxide at comparable reaction conditions as Co-sulfide formed only 2.4% monomer, indicating cobalt oxide is not an active species. The recycling experiment and the catalyst characterization results suggest that CoS is formed during the reaction and is active for C-C cleavage, however the role of CoS₂ cannot be precluded for the reason that the reaction starting with CoS₂ gives a slightly higher amounts of monomers.

CONCLUSIONS

Selective cleavage of interunit C–C linkages of condensed technical lignins has been a longstanding challenge. This study demonstrates that such cleavage of C–C bonds in lignin is possible selectively using an inexpensive cobalt sulfide catalyst. C–C cleavage of a representative C-C linked lignin motif, dimethylguaiacylmethane (DGMG), gives two aromatic monomers with high yield and selectivity at mild conditions and in short reaction time. The reaction for a prolonged time forms non-aromatic products. Methoxy substituent has a little effect to the C–C cleavage, while the dimer becomes unreactive to the C–C cleavage upon dehydroxylation. Depolymerization of a kraft lignin fraction gives lower molecular weight (Mw) soluble lignin species including up to 13% monomer, containing 5 detected functional aromatic monomers.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXX. Experimental procedure for DMGM synthesis and catalysis of DMGM and kraft lignin; analytical methodology for analysis of liquid products; quantification of liquid products; characterization of catalysts; ¹H, ¹³C and HSQC NMR of

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DMGM; GC and GC-MS chromatogram and spectra of products; XRD patterns and deconvoluted XPS spectra; controlled experimental data; structures of monomers and dimers from DMGM and kraft lignins; conversion and yield data.

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ACKNOWLEDGEMENTS

This work was conducted with financial support as part of the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001004. MCT acknowledges the National Science Foundation for supporting kraft lignin fractionation and purification work via ALPHA process (Grant No. CBET-1403873).

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