Chem

Article

Breaking the Limit of Lignin Monomer Production via Cleavage of Interunit Carbon-Carbon Linkages



Lignin, containing a large volume of aromatic functionalities, is the most energydense fraction of renewable biomass. Particularly, conversion of lignin into monocyclic hydrocarbons as commodity chemicals is a highly desirable target. However, this is severally hindered by the presence of stable interunit carboncarbon linkages in native lignin and those formed during lignin extraction. Here, we report a multifunctional Ru/NbOPO₄ catalyst that achieves the first example of catalytic cleavage of both interunit C-C and C-O bonds in lignin in one-pot reactions.



Dong et al., Chem 5, 1–16 June 13, 2019 © 2019 Elsevier Inc. https://doi.org/10.1016/j.chempr.2019.03.007

Lin Dong, Longfei Lin, Xue Han, ..., Stewart F. Parker, Sihai Yang, Yanqin Wang

guoyong@ecust.edu.cn (Y.G.) sihai.yang@manchester.ac.uk (S.Y.) wangyanqin@ecust.edu.cn (Y.W.)

HIGHLIGHTS

Catalytic cleavage of both C–C and C-O bonds in lignin is

The conventional theoretical limitation on lignin monomer production is broken

Excellent activity for C-C bond breakage depends on the unique property of Ru/NbOPO₄

A new method for the hydrogenolysis of lignin into monocyclic hydrocarbons is

Chem

Article

CellPress

Breaking the Limit of Lignin Monomer Production via Cleavage of Interunit Carbon–Carbon Linkages

Lin Dong,^{1,5} Longfei Lin,^{2,5} Xue Han,² Xiaoqin Si,³ Xiaohui Liu,¹ Yong Guo,^{1,*} Fang Lu,³ Svemir Rudić,⁴ Stewart F. Parker,⁴ Sihai Yang,^{2,*} and Yanqin Wang^{1,6,*}

SUMMARY

Conversion of lignin into monocyclic hydrocarbons as commodity chemicals and drop-in fuels is a highly desirable target for biorefineries. However, this is severely hindered by the presence of stable interunit carbon-carbon linkages in native lignin and those formed during lignin extraction. Herein, we report a new multifunctional catalyst, Ru/NbOPO₄, that achieves the first example of catalytic cleavage of both interunit C–C and C–O bonds in one-pot lignin conversions to yield 124%–153% of monocyclic hydrocarbons, which is 1.2–1.5 times the yields obtained from the established nitrobenzene oxidation method. This catalyst also exhibits high stability and selectivity (up to 68%) to monocyclic arenes over repeated cycles. The mechanism of the activation and cleavage of 5–5 C–C bonds in biphenyl, as a lignin model adopting the most robust C–C linkages, has been revealed via *in situ* inelastic neutron scattering coupled with modeling. This study breaks the conventional theoretical limit on lignin monomer production.

INTRODUCTION

Lignin, accounting for 15–40 wt % of lignocellulosic biomass, is the most abundant source of renewable aromatics on earth.^{1–4} The heavily branched 3D network of lignin is constructed from methoxylated phenylpropanoid subunits bridged by various interunit C–O and C–C linkages (accounting for approximately 70% and 30%, respectively) in a completely random order (Figures 1 and S1).^{5–7} C–C bonds have notably higher dissociation energy (226–494 kJ mol⁻¹) than those of C–O bonds (209–348 kJ mol⁻¹) in lignin (Table S1).⁶ Because of its highly robust polymeric structure, the conversion of lignin to small-molecule arenes as commodity chemicals and fuel additives represents a significant challenge for industries and biorefineries.

State-of-the-art processes usually undergo lignin depolymerization via the cleavage of C–O bonds to obtain low-molecular-weight monomers, which can be sequentially upgraded to useful chemicals and fuels.^{1,2} A great deal of effort has been devoted to developing strategies for the depolymerization of lignin.^{8–22} However, the primary products from these processes are mixtures of oxygen-containing compounds with high boiling points, which can hardly be separated by conventional distillation techniques. Moreover, the yields of lignin monomers are limited because of the presence of stable interunit C–C bonds within native lignin or those formed during lignin extraction.²³ Importantly, adding formaldehyde during the pre-treatment of biomass can effectively improve the yield of lignin monomers by preventing the interunit C–C coupling.^{23,24} More interestingly, the emerging "lignin-first"

The Bigger Picture

The conversion of lignin into monocyclic hydrocarbons as commodity chemicals and drop-in fuels is essential for the future of biorefineries. State-of-the-art lignin depolymerization is primarily achieved via cleavage of interunit C-O bonds to form lowmolecular-weight feedstocks. However, these processes can hardly cleave interunit C–C bonds in lignin, and thus, the yields of lignin monomers are heavily restricted. Here, we report a multifunctional catalyst, Ru/ NbOPO₄, that achieves the first example of catalytic cleavage of both interunit C–C and C–O bonds in lignin in one-pot reactions to yield 153% of monocyclic C_6-C_9 hydrocarbons from Kraft lignin, which is 1.5 times the theoretical yield obtained from the established nitrobenzene oxidation (NBO) method. Thus, significantly, this study successfully breaks the conventional limit on lignin monomer production.

Chem

CellPress



Figure 1. View of a Representative Structure of a Lignin Fragment Shows Various Intramolecular Linkages and Schematic Representation of the One-Pot Depolymerization and Hydrodeoxygenation of Lignin into Monocyclic Aromatic Hydrocarbons

The route above the green arrow shows the formation of monocyclic arenes via cleavage of both C–O and C–C linkages.

approaches have shown productions of (near)theoretical amounts of phenolic monomers via solvolytic delignification, offering great promise for high-yield lignin depolymerization.^{4,21,22} However, the cleavage of intrinsic C–C bonds within native and technical lignin remains a long-standing challenge. Very recently, a CoS₂ catalyst has enabled the cleavage of C–C bonds in methylene-linked lignin models.²⁵ However, this catalyst has a limited structural stability and is inefficient to cleave the most robust 5–5 C–C linkages in lignin. Although lignin can be directly converted into volatile hydrocarbons via catalytic hydropyrolysis at typically 650°C,^{26–28} these processes are very energy consuming, and deactivation of catalysts often occurs rapidly because of the coke formation (up to 40%).^{29,30}

Efficient catalytic cleavage of both interunit C–C and C–O linkages in lignin can maximize the lignin monomer production and thus is highly desirable. This is, however, a very challenging task and requires solutions based upon new multifunctional catalysts. Zeolite materials incorporating Brønsted acid sites can catalyze hydrocarbon cracking in petroleum refineries.^{31,32} Phosphate-based materials containing strong Brønsted acid sites can protonate benzene rings and thus facilitate the cleavage of C–C bonds.^{33,34} However, these materials alone have poor activity in cleaving C–O bonds in lignin.³⁵ Meanwhile, the emerging NbO_x-supported catalysts have exhibited unique activities in cleaving C–O bonds in biomass to yield fully deoxygenated compounds.³⁶

Here, we report a mesoporous multifunctional catalyst, Ru/NbOPO₄, that combines the NbO_x species and phosphates containing strong Brønsted acid sites and thus enables the efficient cleavage of both interunit C–O and C–C linkages in lignin. Significantly, the one-pot conversion of lignin over Ru/NbOPO₄ integrates the depolymerization of lignin, the hydrogenolysis of depolymerized compounds, and the cleavage of interunit C–C linkages and achieves optimal production of monocyclic hydrocarbons. Theoretical yields of intrinsic lignin monomers have been determined from the established nitrobenzene oxidation (NBO) method (Note S1)^{23,37,38} and serve as the 100% standard in this report. Here, the ratio of molar yields (RMY) is defined as (molar yield of monocyclic compounds over Ru/NbOPO₄)/(molar yield of monocyclic compounds from NBO) × 100%. When RMY above 100% is obtained, it suggests the recovery of additional monocyclic compounds from depolymerized dimer and oligomer products via the cleavage of interunit C–C linkages (Figure 1). The one-pot conversion of lignin over the Ru/NbOPO₄ catalyst has produced liquid ¹Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

²School of Chemistry, University of Manchester, Manchester M13 9PL, UK

³State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, China

⁴ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, UK

⁵These authors contributed equally ⁶Lead Contact

*Correspondence:

guoyong@ecust.edu.cn (Y.G.), sihai.yang@manchester.ac.uk (S.Y.), wangyanqin@ecust.edu.cn (Y.W.) https://doi.org/10.1016/j.chempr.2019.03.007

Chem

CelPress

monocyclic hydrocarbons with an RMY up to 153% as well as an exceptional arene selectivity of 68%. Furthermore, the unique activity of Ru/NbOPO₄ to crack the interunit C–C bonds has been confirmed in lignin dimer models (e.g., biphenyl, diphenylmethane, and diphenylethane), where high yields of monocyclic aromatics have been obtained. A combined inelastic neutron scattering (INS) and density functional theory (DFT) analysis unambiguously confirmed the strong adsorption with preferred orientation, activation, and hydrogenolysis of biphenyl on the surface of Ru/NbOPO₄. To the best of our knowledge, this is the first example of using INS and DFT to study the mechanism of C–C bond activation in biomass conversions.

RESULTS

One-Pot Conversion of Lignin into Monocyclic Hydrocarbons

Mesoporous NbOPO₄ was prepared from a hydrothermal reaction and a loading of 5 wt % Ru conducted via wetness impregnation (Note S2). The total acid amount and Brunauer-Emmett-Teller (BET) surface area of activated Ru/NbOPO4 were determined to be 980 $\mu mol~g^{-1}$ and 235 $m^2~g^{-1},$ respectively, and the pore size distribution was centered at 3.5 nm (Figure S2). The mesopores and high porosity of the catalyst can promote reactions taking place at the solid-solid interface and have a positive effect on the mass transfer of substrates and reaction intermediates. Kraft lignin, typically produced from chemical pulping processes, has a highly condensed and cross-linked (via interunit C-C bonds) network. Its intrinsic monomer units were determined to be 1,040 μ mol g⁻¹ from the NBO method (Tables S2 and S3), which is widely used in the literature as a standard protocol for analyzinig lignin monomers connected by C–O bonds (including but not limited to β –O–4 linkage).^{23,38,39} The C-C linkage in lignin cannot be cleaved in the NBO method, thus making the comparison straightforward for the present study. It has been reported that the theoretical amount of lignin monomers coincides with the square of the fraction of ether bonds in the lignin structure, and that of birch lignin varies from 45% to 58%.^{7,22} With the NBO method, on the basis of the molar content of S, G, and H units in birch lignin, the maximum amount of lignin monomers was found to be within the range of 52%-57% (Table S2, entry 4), highly consistent with the reported results. The onepot conversion of Kraft lignin was first tested over the Ru/NbOPO₄ catalyst in dodecane at 310°C under 0.5 MPa H₂ for 40 h. Interestingly and surprisingly, a very high yield of monocyclic hydrocarbons (1,594 μ mol g⁻¹/14.5 wt %) was obtained with a C₆-C₉ arene selectivity of 68% (Table 1, entry 1; Table S4, entry 4; Table S5). This gives an RMY of 153%, indicating a 53% additional recovery of monocyclic hydrocarbons via the cleavage of interunit C-C linkages in Kraft lignin. Next, enzymic corncob, pine, and birch lignin (representing grasses, softwood, and hardwood lignin, respectively, Table S2 and Note S3) were employed as feedstocks (Table 1, entries 3-5; Table S6). The RMY for conversions of enzymic, pine, and birch lignin were 147%, 151%, and 124%, respectively, confirming the cleavage of interunit C-C linkages in all cases. Importantly, high selectivities to monocyclic arenes ranging from 62% to 67% were obtained throughout, demonstrating the general applicability of this multifunctional catalyst and one-pot approach to producing monocyclic arenes. In addition, the comparison of the activity and selectivity with early reported literature in the one-pot conversion of lignin is also summarized in Figure S3 and Note S4.

Stability Tests

To investigate the stability of Ru/NbOPO₄, we conducted three consecutive conversions of Kraft lignin by using the recycled catalyst. Negligible changes in reaction yield or arene selectivity were observed (Figure 2; Table S7). For example, the yield of monocyclic hydrocarbons and arene selectivity on the third run were 1,588 μ mol g⁻¹ and 66%, comparable to those (1,594 μ mol g⁻¹ and 68%) achieved

Chem

CellPress

Entry	Lignin	Product Distribution (μ mol·g ⁻¹)									Total Amount	Selectivity to	RMY (%) ^c
		C ₆ -C ₉ Arenes				C ₆ C ₉ Cycloalkanes					(µmol g ⁻ '/wt %)	Arenes (%) ⁶	
			\bigcirc			\bigtriangledown	\bigcirc	\bigcirc					
1	Kraft	524	389	103	67	209	42	167	67	26	1,594/14.5	68	153
2 ^d	Kraft	204	262	146	42	56	88	150	88	19	1,055/10.1	62	101
3	enzymic	651	323	387	77	69	98	203	266	61	2,135/20.3	67	147
4	pine	1,179	640	177	138	285	211	448	111	65	3,254/29.3	66	151
5	birch	796	877	251	191	254	191	487	189	158	3,394/31.9	62	124

Table 1. Summary of the Products Distribution from the One-Pot Conversion of Lignin over the Ru/NbOPO4 Catalyst^a

 $^a Reaction$ conditions: 0.1 g lignin, 0.2 g 5% Ru/NbOPO_4, 5 mL dodecane, and 0.5 MPa H_2 at 310 $^\circ C$ for 40 h.

^bSelectivity to arenes = (total amount of arenes)/(total amount of hydrocarbons) \times 100%.

^cRatio of molar yields (RMY) = (molar yield of monocyclic compounds over Ru/NbOPO₄)/(molar yield of monocyclic compounds from NBO) × 100% = (total amount of monocyclic hydrocarbons over Ru/NbOPO₄)/(theoretical amount of monocyclic hydrocarbons from NBO) × 100%. The theoretical hydrocarbon amounts of Kraft lignin, enzymic lignin, pine lignin, and birch lignin are 1,040, 1,448, 2,162, and 2,741 μ mol g⁻¹, respectively. Theoretical hydrocarbon amounts were calculated by the NBO method as described in Table S2 and Note S1.

^dReaction conditions: 0.1 g lignin, 0.2 g 5% Ru/NbOPO₄, 5 mL dodecane, and 0.5 MPa H₂ at 250°C for 20 h.

with a fresh catalyst. The stability test was also conducted with 100 wt % catalyst loading in four consecutive recycling runs (Table S8; Note S5), where the catalytic activity reduced after the first run and remained the same for the following runs. X-ray diffraction (XRD), transmission electron microscopy (TEM), and chemical analysis further confirmed the absence of notable structural change, aggregation of Ru particles, and leaching of Ru, respectively, for the used catalyst (Figures S4 and S5; Table S9). These results demonstrate the excellent stability of Ru/NbOPO₄ in this one-pot process. In addition, the effect of S element in Kraft lignin was also studied by control experiments, suggesting that the S element in Kraft lignin has little effect on the catalytic activity (Table S10; Note S6).

Analysis of the Reaction Pathways

To investigate the reaction pathways, we converted Kraft lignin at 250°C for 20 h (Table 1, entry 2; Table S4; Note S7) and isolated and analyzed reaction intermediates by 2D heteronuclear single-quantum coherence nuclear magnetic resonance (HSQC NMR). Compared with NMR signals for the raw lignin, those for A (β -O-4 linkages), B (β -5 linkages), and C (β - β linkages) decreased significantly in the side-chain regions after the reaction, and the presence of G and H subunits in the reaction residue was negligible (Figure S6). Elemental analysis shows only a minor oxygen content (<0.8 wt %) in the reaction intermediates, further suggesting the near-complete oxygen removal during the initial reaction. Meanwhile, bicyclic aromatic hydrocarbons (e.g., biphenyl and diphenylethane) were also detected (Figure S7), indicating that the activation and cleavage of interunit C-C bonds in depolymerized compounds require additional energy input, consistent with the difference in their bond dissociation energies (Table S1). The mass yield of total monocyclic compounds at 250°C for 20 h was only 10.1 wt % (Table 1, entry 2), and that can be increased to 14.5 wt % at 310°C for 40 h via further cleavage of C-C linkages in depolymerized compounds.

Catalytic Cleavage of C5-C5 Linkages in Lignin Model Compounds

Among all interunit C–C linkages in lignin, the 5–5 bond between two phenyl groups accounts for the highest portion in lignin (40%–50% in softwood and 25%–40% in

Chem





Figure 2. Comparison of C₆–C₉ Reaction Products and Arene Selectivity in Three Consecutive Recycling Runs of One-Pot Conversion of Kraft Lignin over the Ru/ NbOPO₄ Catalyst

Reaction conditions: 0.1 g Kraft lignin, 0.2 g 5% Ru/NbOPO₄, 5 mL dodecane, and 0.5 MPa H_2 at 310°C for 40 h.

hardwood on the basis of all C-C linkages) and has the strongest dissociation energies of 481–494 kJ mol⁻¹. Therefore, biphenyl is selected for in-depth investigation as a model compound for C-C cleavage.^{7,40} To closely monitor the intermediates, we conducted the reaction at a reduced temperature of 280°C (Figure 3). Initially, phenylcyclohexane (1) was found to accumulate rapidly to 73% within 1 h and then gradually convert to benzene (2) and cyclohexane (3) as the reaction proceeded. This indicates that the partial hydrogenation of biphenyl occurred to activate the C_5-C_5 linkage from the sp²-sp² to sp²-sp³ bond, thus effectively reducing the bond dissociation energy. Similar product distribution was obtained when 1 was used as the substrate, confirming 1 as the primary intermediate in the conversion of biphenyl (Figure S8). Interestingly, a small amount of bicyclohexyl (4) was observed after 2 h, and no further conversion of 4 occurred with prolonged reaction time. Indeed, no product was detected in the hydrogenolysis of 4 or dodecane under the same reaction conditions (Figures 4A and 4B), indicating that $Ru/NbOPO_4$ has a poor activity to cleave the Caliphatic-Caliphatic bonds, although they have considerably lower bond dissociation energy. Comparison of the Fourier transform infrared spectroscopy (FTIR) of adsorbed biphenyl, 1, 4, and dodecane on $Ru/NbOPO_4$ showed that the catalyst had much weaker binding to aliphatic hydrocarbons than that to aromatic ones (Figure S9; Note S8), indicating that the adsorption of substrates on the catalyst surface plays an important role in its activation.

Interestingly, small amounts of (1-methylcyclopentyl)-benzene (5) and (1-methylcyclopentyl)-cyclohexane (6) were also detected, indicating the presence of isomerizations in this one-pot process. The hydrogenation of biphenyl can generate phenylcyclohexene, which undergoes isomerization to give 5. 5 can be further cracked into 2 and methylcyclopentane (7) (Figure 5, route 2). On the other hand, 7 can also be obtained from the isomerization of 3 (Figure 5, route 1; Figure S10). Thus, the conversion of biphenyl over Ru/NbOPO₄ first undergoes partial hydrogenation to 1 or phenylcyclohexene, which is then converted via three plausible routes (Figure 5). In route 1, 1 is directly cracked into 2 and 3; the minority of the latter is isomerized to 7. In route 2, biphenyl is first hydrogenated to phenylcyclohexene and then isomerized and hydrogenated to produce 5, which is finally cracked to 2 and 7. In route 3, further hydrogenation of 1 produces 4, which cannot undergo further conversion. It is worth noting that the isomerization in routes 1 and 2 has a very minor contribution to the final products, and the direct cracking of 1 in route 1 is the dominant pathway, resulting in the efficient production of monocyclic hydrocarbons.

To investigate the role of the density of acid sites, we converted biphenyl over Ru/ Nb_2O_5 (Table 2, entries 2 and 3). Compared with Ru/NbOPO₄, Ru/Nb₂O₅ showed significantly reduced activity for C–C cleavage, with only 3.5% yield of monocyclic products, whereas upon the addition of trifluoromethanesulfonic acid, the yield of monocyclic greatly increased to 38.0%, confirming the important role of Brønsted

Chem

CellPress



Figure 3. Product Distributions versus Reaction Time for the Conversion of Biphenyl over the Ru/ NbOPO₄ Catalyst

Views of variation of the yield (A) and selectivity (B) for all possible intermediates and products as shown in (C). Reaction conditions: 0.2 g biphenyl, 0.1 g 5% Ru/NbOPO₄, 2 g dodecane, and 0.5 MPa H_2 at 280°C.

acids. Another control experiment of the hydrogenolysis of biphenyl over the catalyst support, NbOPO₄, was conducted under the same reaction condition, and no product was detected (Table 2, entry 4). This result indicates that Ru nanoparticles serving as active sites for the dissociation of hydrogen molecules are also important, consistent with those reported in literature.^{41,42}

The performance of Pd/NbOPO₄, Pt/NbOPO₄, and Rh/NbOPO₄ on C-C cleavage of biphenyl was also tested (Table 2, entries 5-7). Over Pd/NbOPO₄, the yield of benzene and cyclohexane was 16.3% and 12.3%, respectively, lower than that of Ru/ NbOPO₄ (24.4% and 19.1%, respectively), and the main product was bicyclohexyl (42.1%). Over Pt/NbOPO₄, the main product was also bicyclohexyl (54.2%), and cyclohexane and benzene were produced in 18.5% and 1.3% yields, respectively. The notably stronger activity for hydrogenation over Pd and Pt catalysts than Ru catalysts^{14,43} greatly promoted further hydrogenation of the primary reaction intermediate (phenylcyclohexane) and thus hindered the cleavage of C-C bonds, thereby leading to low yields of monocyclic products. Over the Rh/NbOPO4 catalyst, the yield of monocyclic products reached 39.4%, but the arene selectivity was significantly lower than that of Ru/NbOPO₄, indicating that Rh/NbOPO₄ can promote further hydrogenation of benzene into alkanes. Thus, the unique activity of Ru-based analog is attributed to its moderate ability for hydrogenation to enable the partial hydrogenation of biphenyl to phenylcyclohexane while preventing any further hydrogenation of the intermediate and product. It is worth noting that all catalysts (Ru, Pd, Pt, or Rh/NbOPO₄) are inactive for C-C cracking of bicyclohexyl under the same conditions.

HZSM-5 is widely used for cracking and hydrocracking processes in petroleum refineries,⁴⁴ and Ru/HZSM-5 has also been studied for the conversion of biphenyl (Table 2, entry 8). The yield of monocyclic hydrocarbons over Ru/HZSM-5 was only 8.8%, but phenylcyclohexane was produced in 57.3% yield together with small amounts of C₁-C₄ products in the gas phases. This result gives sharp comparisons to Ru/NbOPO₄, which can effectively prevent the deep cracking of substrate and intermediates and thus lead to the optimal production of monocyclic arenes.

Chem





Figure 4. The Conversion of Hydrocarbons over the Ru/NbOPO₄ Catalyst

(A–D) Product distributions for the conversion of bicyclohexyl (A), solvent dodecane (B), diphenylmethane (C), and diphenylethane (D).

(E) Schemes of selective hydrogenolysis of three lignin model compounds over the $\mbox{Ru/NbOPO}_4$ catalyst.

Reaction conditions: 0.2 g reactant, 0.1 g 5% Ru/NbOPO₄, 2 g dodecane, and 0.5 MPa H₂ at 280°C for 12 h. Product yield was calculated with the following equations: yield of the monocyclic compound = (molar amount of the monocyclic compound)/(molar amount of the substrate)/2 × 100%; yield of the bicyclic compound = (molar amount of the bicyclic compound)/(molar amount of the substrate) × 100%.

Catalytic Cleavage of Other C-C Linkages in Lignin Model Dimers

Conversions of diphenylmethane and diphenylethane, as the α -1 and β -1/ β -5 lignin models, respectively, were also studied. The conversion of diphenylmethane gave benzene (31.7%) and toluene (10.8%) as two main products together with the presence of a small amount of ring-saturated products (Figure 4C). For diphenylethane, the main products were benzene and ethylbenzene (12.4% and 6.7%, respectively), and there was a small amount of toluene (2.7%) (Figure 4D). These results confirm that Ru/NbOPO₄ truly has activity for the selective and direct hydrogenolysis of C_{aromatic}–C bonds (Figure 4E). The carbon balance was 88%~92%, and the discrepancies are due to (1) the adsorption of substrate, intermediate, and product on the catalyst surface, (2) a small amount of alkane products in the gas phase, and (3) a small loss of product during the extraction and transfer of product during analysis.

INS Studies on Adsorption, Activation, and Hydrogenolysis of Biphenyl

The selective cleavage of interunit C–C linkages in depolymerized lignin components and simultaneous maintenance of the aromatic functionalities of phenyl rings leads to the optimal production of monocyclic arenes in this study. Direct

Chem





Figure 5. Proposed Reaction Network of the Conversion of Biphenyl over the Ru/NbOPO_4 Catalyst

The direct cracking of phenylcyclohexane in route 1 is the dominant pathway.

visualization of the interaction between adsorbed biphenyl and the catalyst (Ru/ NbOPO₄) surface is crucial to understanding the molecular details of adsorption, activation and hydrogenolysis of biphenyl into monocyclic hydrocarbons. INS is a powerful neutron spectroscopy technique for investigating the dynamics (particularly for the deformational and conformational modes) of biphenyl, and the DFT calculation of INS spectra is straightforward. Therefore, we combined *in situ* INS and DFT calculations to investigate the molecular-binding properties of the biphenyl-Ru/NbOPO₄ system to reveal the conversion mechanism of biphenyl.

The INS spectrum of bare Ru/NbOPO₄ catalyst gave a clean background with a broad feature centered at 1,100 cm⁻¹, indicating the presence of surface hydroxyl groups (Figures S11 and S12; Note S9). In comparison, on the adsorption of biphenyl at 220°C, the INS spectrum showed a significant increase in total intensity, demonstrating the binding of biphenyl to the catalyst surface (Figure S11). The INS spectrum of solid biphenyl was also collected and analyzed via DFT calculations (Figure S13; Table S11), allowing a full assignment of the spectral features for biphenyl.

Comparison of the difference of INS spectra before and after biphenyl adsorption on the catalyst (that is, signals for adsorbed biphenyl) and that of the solid biphenyl showed a number of marked changes (Figure 6A). Peaks at low energy (below 120 cm⁻¹), assigned to the translational and rotational modes of biphenyl, shifted to lower energy with a continuum profile, suggesting that adsorbed biphenyl molecules are disordered over the catalyst surface with hindered motions as a result of the strong binding to the catalyst. The modes of C₅–C₅ out-of-plane and in-plane bending (135 and 189 cm⁻¹, respectively) disappeared completely upon adsorption on the catalyst surface, suggesting that the biphenyl molecule adsorbed onto the catalyst with a flat position. Meanwhile, the peak at 443 cm⁻¹ (assigned to C₂ and C₅ out-of-plane wagging) decreased significantly and shifted to higher energy at 488 cm⁻¹ (Δ = 45 cm⁻¹); this notable blue shift is consistent with the strong binding of phenyl plane on the catalyst surface. The intensities of deformational modes of benzene rings at 628, 736, and 986 cm⁻¹ also reduced dramatically. These results strongly indicate that both benzene rings of biphenyl adsorbed on the catalyst.

Chem

CellPress

Entry	Catalyst	Yield (C %)	Conversion (C %)							
		Monocyclic	:		Dicyclic					
		\bigcirc	\bigcirc	\checkmark			\mathcal{F}	P		
1	5% Ru/NbOPO ₄	24.4	19.1	3.3	25.4	13.6	0.9	5.7	97.0	
2	5% Ru/Nb ₂ O ₅	1.1	2.3	0.1	55.8	24.2	0.5	4.9	97.8	
3 ^c	5% Ru/Nb ₂ O ₅ TfOH	20.1	5.0	12.9	29.8	15.7	0.2	2.0	98.2	
4	NbOPO ₄	0	0	0	0	0	0	0	0	
5	5% Pd/NbOPO ₄	16.3	12.3	3.6	5.5	42.1	3.1	6.6	>99.9	
6	5% Pt/NbOPO ₄	1.3	18.5	1.4	2.1	54.2	1.7	5.6	>99.9	
7	5% Rh/NbOPO ₄	3.5	33.6	2.3	21.7	15.8	2.7	7.5	98.8	
8 ^d	5% Ru/HZSM-5	4.9	3.1	0.8	57.3	4.7	1.4	0.3	95.3	

Table 2. Summary of the Products Yields from the Conversion of Biphenyl over Different Catalysts^a

^aReaction conditions: 0.2 g biphenyl, 0.1 g catalyst, 2 g dodecane, and 0.5 MPa H_2 at 280°C for 12 h.

^bProducts yields were calculated with the following equations: yield of the monocyclic compound = (molar amount of the monocyclic compound)/(molar amount of the substrate)/2 × 100%; yield of the bicyclic compound = (molar amount of the bicyclic compound)/(molar amount of the substrate) × 100%.

 c Reaction conditions: 0.2 g biphenyl, 0.1 g catalyst, 0.05 g trifluoromethanesulfonic acid, 2 g dodecane, and 0.5 MPa H₂ at 280 $^{\circ}$ C for 12 h.

 $^{\rm d}\text{C}_1\text{--}\text{C}_4$ alkanes were detected in the gas phases.

Meanwhile, the wagging (677, 1,100, and 1,281 cm⁻¹), scissoring (1,215 cm⁻¹), and rocking (1,480 cm⁻¹) modes of C–H groups on both benzene rings disappeared, and INS peaks at 913 cm⁻¹ (C–H wagging), 1,045 cm⁻¹ (C–H rocking), and 1,178 cm⁻¹ (C–H scissoring) notably decreased in intensity. The peaks at 245 and 392 cm⁻¹, corresponding to the twisting mode of the C–C bond within benzene rings, shifted to 269 and 366 cm⁻¹, respectively. The peak at 331 cm⁻¹ (assigned to the intra-ring stretching mode of benzene) shifted to lower energy at 313 cm⁻¹ (Δ = 18 cm⁻¹). These changes suggest that the adsorbed biphenyl molecules are partially protonated by the acid sites residing on the catalyst surface (e.g., hydroxyls) and the intermediate carbocation formed (Figure S10).⁴⁵ These results are in good agreement with the *in situ* FTIR experiments, where a red shift (Δ = 28 cm⁻¹) was observed for the C₅–C₅ stretching mode on adsorption (Figure S14; Note S8).

The adsorbed biphenyl molecules on Ru/NbOPO₄ underwent a first catalytic conversion in H₂ at 170°C for 6 min. Comparison of the INS spectra of the first reacted and adsorbed biphenyl showed a few changes (Figure 6B). The peaks at 736 and 986 cm⁻¹ (ring deformational mode of phenyl group) disappeared upon reaction in H₂, and the peaks at 269, 313, and 366 cm⁻¹ shifted to 275, 295, and 358 cm⁻¹, respectively, indicating the formation of phenylcyclohexane via the further hydrogenation of the intermediate carbocation. The spectrum for reacted catalyst also showed the appearance of several new features at 242, 432, 460, 512, 895, 1,274, 1,348, and 1,456 cm⁻¹, which are all consistent with the spectrum of phenylcyclohexane. In contrast, the INS spectrum also confirmed the absence of bicyclohexyl on catalyst surface (Figure S15), suggesting that only one benzene ring on biphenyl is hydrogenated during the initial reaction.

To promote the further conversion of phenylcyclohexane, we carried out a second hydrogenation by feeding a 5% H_2 /He stream at 270°C for 6 min. The cell outlet was monitored continuously via mass spectrometry (MS), which confirmed the

Chem

CellPress



Figure 6. Inelastic Neutron Scattering Spectra for Ru/NbOPO₄ on the Adsorption and Catalytic Conversion of Biphenyl

All spectra shown here are difference spectra; raw data are shown in Figures S9 and S10. INS spectra of the reduced catalysts were used throughout for calculations of the corresponding difference spectra. No abscissa scale factor was used throughout this report for INS calculations. INS spectra for condensed biphenyl, phenylcyclohexane, and benzene in the solid state at 10 K were included accordingly for a direct comparison of the vibrational modes between the adsorbed or bound molecules and the free, intact molecules. Two hydrogenation reactions of adsorbed biphenyl were conducted in pure and diluted (5%) H_2 steams. Where no error bars are visible, these are smaller than the symbols used to represent the data points.

(A) Comparison of INS spectra for solid and adsorbed biphenyl on Ru/NbOPO₄.

(B and C) INS spectra for Ru/NbOPO $_4$ during the first (B) and second (C) catalytic conversions of biphenyl.

(D) Views of selected C-C vibration models of biphenyl.

Chem

CellPress

presence of benzene as the main product. Comparison of the INS spectra of the first and second reacted biphenyl on Ru/NbOPO₄ showed that the INS peaks for phenylcyclohexane significantly reduced in intensity (436, 496, 1,348, and 1,453 cm⁻¹) or completely disappeared (242, 464, and 895 cm⁻¹) on the second reaction (Figure 6C), indicating that high temperature greatly promoted the cleavage of C_5-C_5 bonds in adsorbed phenylcyclohexane on Ru/NbOPO₄. New features appeared at 609 and 980 cm⁻¹, and the peaks at 405, 702, 857, and 1,185 cm⁻¹ increased in intensity, fully consistent with the formation of benzene.

To confirm the adsorption domain, we also collected INS data for biphenyl-adsorbed catalyst support NbOPO₄ (Figure S16), and the INS spectra were fully consistent with that of Ru/NbOPO₄, indicating that the primary adsorption sites of Ru/ NbOPO₄ reside on NbOPO₄ and that Ru particles have little effect on adsorption. Similar findings were also obtained from an in situ FTIR experiment (Figure S17). Furthermore, the conventional C-C cracking catalyst, HZSM-5, was also selected for the study of biphenyl adsorption by INS and diffuse reflectance infrared Fourier transform (DRIFT) (Figures S18 and S19). The INS data confirmed the strong binding of biphenyl on HZSM-5 surface, and small differences between adsorbed biphenyl on HZSM-5 and NbOPO₄ were observed. The ring deformation mode of adsorbed biphenyl on NbOPO₄ observed at 628 $\rm cm^{-1}$ disappeared upon adsorption on HZSM-5. The C-H wagging mode of biphenyl at 677 cm⁻¹ disappeared upon adsorption on NbOPO₄, whereas this was clearly visible for HZSM-5. In situ DRIFT data revealed a large red shift (Δ = 100 cm⁻¹) for the C–H stretching mode of adsorbed biphenyl over NbOPO₄, whereas the red shift was only by 10 cm⁻¹ over HZSM-5 (Figure S19). These results confirm that NbOPO₄ shows stronger adsorption of biphenyl than HZSM-5.

The adsorption of key intermediate (phenylcyclohexane) on NbOPO₄ and HZSM-5 was also studied by INS to reveal the origin of their distinct catalytic activities. The DFT-calculated INS spectrum of phenylcyclohexane agreed very well with the experimental data (Figure S20; Table S12). Comparison of the difference in INS spectrum before and after phenylcyclohexane adsorption on NbOPO₄ (that is, signals for adsorbed phenylcyclohexane) and that of the solid biphenyl showed a number of changes (Figure S21). Peaks at low energy (below 120 cm⁻¹), assigned to the translational and rotational modes of phenylcyclohexane, shifted to lower energy with a continuum profile, suggesting that the adsorbed phenylcyclohexane molecules were disordered over the catalyst surface with hindered motions as a result of the strong binding to the catalyst. A number of INS peaks of phenylcyclohexane decreased in intensity on adsorption on NbOPO₄, including bands at 297 cm⁻¹ (wagging of C_2 , C_4 , and C_6 in benzene ring), 530 cm⁻¹ (wagging of C_2 and C_5 in benzene ring), and 848 and 996 cm⁻¹ (wagging of C-H groups on benzene ring), indicating that the adsorption of phenylcyclohexane was primarily via its benzene ring. The wagging modes (247 cm⁻¹) of C₇ and C₁₀ of the cyclohexane ring disappeared completely upon adsorption, and the intensities of C-C twisting modes (237 cm⁻¹) in the cyclohexane ring greatly reduced, indicating the hindrance of motion of the cyclohexane ring on adsorption. In contrast, the comparison of INS spectra of adsorbed phenylcyclohexane on HZSM-5 and that of solid phenylcyclohexane showed only small decreases in the intensity of peaks at 247, 281, and 297 cm^{-1} . This result suggests that adsorbed phenylcyclohexane was weakly bound on the surface of HZSM-5 with similar motions to the solid state and could easily desorb. This is in excellent agreement with the catalysis result, where phenylcyclohexane was obtained as the main product over the Ru/HZSM-5 catalyst. Thus, the INS study confirms that although biphenyl can strongly adsorb on both NbOPO₄

Chem

CellPress

and HZSM-5, the former is also able to provide strong adsorption to the intermediate, phenylcyclohexane, thus leading to the selective C–C cleavage to produce monocyclic products (Figure S22).

This INS study confirmed that (1) both benzene rings of biphenyl strongly adsorb on the catalyst surface with a flat orientation, and on adsorption, benzene rings are protonated and the intermediate carbocation is formed; (2) hydrogenation of one benzene ring of biphenyl occurs rapidly in the presence of H₂ to give phenylcyclohexane adsorbed on the catalyst via its phenyl group; and (3) C_5-C_5 bonds are then efficiently cleaved on Ru/NbOPO₄, and the volatile products readily desorb from the catalyst surface, thus preventing the further hydrogenation of reaction intermediates and products and driving the formation of arenes. Therefore, the catalytic conversion of biphenyl follows adsorption, binding, protonation, partial hydrogenation and cleavage of C_5-C_5 linkages, and the catalyst Ru/NbOPO₄ plays an important role in the optimal production of monocyclic aromatics.

DISCUSSION

Much current research on lignin conversion is centered on its depolymerization via cleavage of C-O bonds. Interunit C-C bonds have higher dissociation energies, but their cleavage is critical if the production of low-molecular-weight commodity chemicals and jet fuels from lignin is to be improved. We designed a multifunctional catalyst, Ru/NbOPO₄, by integrating the Brønsted acid sites onto the emerging NbO_x support, coupled with the moderate hydrogenation ability of Ru centers, to enable the cleavage of both interunit C-O and C-C linkages to maximize the lignin monocyclic hydrocarbon production. Exceptional yields (up to 153% compared with those of intrinsic lignin monomer units) of monocyclic hydrocarbons were obtained from the one-pot conversion of various types of lignin. This approach also showed complete removal of oxygen content from lignin and exhibits high selectivity to arene products. Detailed studies using lignin models, including biphenyl, diphenylmethane, and diphenylethane, over multiple catalysts confirmed the unique activity of Ru/NbOPO₄ on the selective cleavage of interring C-C linkages. In situ INS and modeling studies confirmed that the excellent activity of Ru/NbOPO4 originates from a combination of strong adsorption and a synergistic effect between Ru, NbO_x species, and acid sites on the catalyst surface. Ru particles, NbO_x species, and acid sites promoted the dissociation of hydrogen, the strong adsorption of substrates and intermediates, and the partial protonation and activation of adsorbed substrates (e.g., biphenyl), respectively, thus driving the entire reaction.

Zeolite-based catalysts currently dominate the state-of-the-art petroleum refineries for hydrocarbon cracking and pyrolysis-based biorefineries to produce small-molecule feedstock chemicals.³¹ Significantly, the activity of Ru/NbOPO₄ is distinct from that of conventional zeolite-based catalysts. This new one-pot process for lignin conversion offers efficient cleavage of both interunit C–C and C–O cleavages and effectively prevents the deep C–C cracking of low-molecular-weight products. Thus, it results in the isolation of desirable liquid C_6 – C_9 monocyclic hydrocarbons under mild conditions and successfully breaks the conventional theoretical limit on lignin monomer production.

EXPERIMENTAL PROCEDURES

Catalytic Reactions and Analysis of Products

The detailed reaction conditions are described in the figure captions and table footnotes. The one-pot conversion of lignin was conducted in a 25 mL stainless-steel

Chem

CelPress

autoclave reactor. In a typical reaction, lignin (0.10 g), catalyst (0.20 g), and dodecane (5 mL) were filled into the reactor, which was then sealed, purged three times with H₂, and charged to an initial pressure of 0.5 MPa with H₂. The reactor was heated to a target temperature, and the reaction conducted with magnetic stirring. After the reaction, the reactor was quenched in an ice-water bath, and the reaction mixture was centrifuged to separate the catalyst. The organic phase was gualitatively analyzed by gas chromatography-mass spectrometry (GC-MS) (Agilent 7890A-5975C) and quantitatively analyzed by a GC-flame ionization detector (Agilent 7890A) with an HP-5 column. The column temperature began at 50°C (held for 5 min) and was then raised at 10°C min⁻¹ to 250°C (held for 1 min); the total running time was 26 min. Pentadecane was used as an internal standard for the quantification of the liquid products. For the stability test, after each reaction, the used catalyst was isolated by centrifugation, washed with ethanol to remove the unreacted lignin, and dried at 80°C in air overnight before the next run. The theoretical yield of lignin monocyclic units was determined by the established NBO method (Note S1).^{23,37,38} The conversion of lignin models and product analysis were conducted with the same method.

INS Experiments

INS spectra were recorded on the TOSCA spectrometer at the ISIS Facility at the STFC Rutherford Appleton Laboratory (UK). TOSCA is an indirect geometry crystal analyzer instrument that provides a wide dynamic range (16–4,000 cm⁻¹) with resolution optimized in the 50–2,000 cm⁻¹ range.⁴⁶ All INS spectra for the catalysis system were collected after the sample was cooled and stabilized at temperatures below 30 K.

In a typical experiment, the Ru/NbOPO₄ catalyst (22.84 g) was loaded into a flowtype stainless-steel cell that can also be used as a static cell with all valves closed. Similar amounts of catalysts were used for studies of NbOPO₄ and HZSM-5. The Ru/NbOPO₄ catalyst used here had a 5 wt % loading of Ru. The sample was heated at 300°C (5°C min⁻¹ ramping) under He for 3 h to remove any remaining trace water before the experiment. The sample was cooled to room temperature, and a weight loss of 0.89 g was noted as a result of the loss of adsorbed water. The activated catalyst was then reduced by heating under a H₂ flow at 250°C for 3 h. The samples were cooled to <30 K during data collection by a closed-cycle refrigerator cryostat. The procedure of the in situ catalysis experiment with the INS measurements is summarized in Figure S23. To study the reaction mechanism, biphenyl was used as a 5-5 linked lignin model compound. Adsorption of biphenyl was carried out by flowing hot biphenyl vapor diluted in He (1.1 bar, 0.15 L min⁻¹; this flow condition was used throughout the study) over the catalyst at 220°C for 2.5 h, and the exhaust gas was monitored via MS. Before the data collection, the cell was flushed with dry He to remove weakly bound biphenyl molecules. The adsorbed biphenyl underwent the first catalytic conversion in pure H₂ flow for 6 min at 170°C. The cell was then flushed with He to remove weakly bound products and free H₂, sealed, and cooled for INS collection. After the data collection, H_2 (5%) was introduced to the cell for 6 min at 270°C for the second catalytic reaction to occur, and the production of benzene was observed instantly by MS. The cell was then flushed with He again, sealed, and cooled for INS collection to detect the presence of possible reaction intermediates. INS spectra of pure solid compounds for both starting material and reaction products were collected at 10 K. The amount of each sample in the neutron beam was 1.3 g (biphenyl), 2.6 g (phenylcyclohexane), 2.8 g (bicyclohexyl), and 8.1 g (benzene).

Chem

CellPress

In Situ Diffuse Reflectance FTIR

The DRIFT spectra were recorded with a Nicolet NEXUS 670 FTIR spectrometer equipped with an *in situ* reaction chamber and a liquid N₂ cooled high-sensitivity mercury cadmium telluride detector. Prior to the FTIR studies, about 20 mg of the catalyst was finely ground and placed in the chamber. The procedure of the *in situ* biphenyl adsorption experiment with the FTIR measurements is summarized in Figure S24. Before adsorption, the catalysts were activated in flowing He at 300°C for 1 h to remove any remaining trace water and then reduced in flowing H₂ at 250°C for 1 h and decreased to 220°C to collect the background spectra. For the adsorption of biphenyl, it was fed into the chamber by flowing biphenyl vapor in He for 0.5 h; then, the chamber was flushed with dry He at 220°C for 1 h to remove physical or weakly adsorbed molecules, and finally the spectra were recorded with a resolution of 4 cm⁻¹ and an accumulation of 64 scans. The adsorption of phenylcyclohexane, bicyclohexyl, and dodecane was conducted in the same method (Figure S9; Note S8). All spectra were used after subtracting the background.

DATA AND SOFTWARE AVAILABILITY

The data supporting the findings of this study are available within the article or available from the authors upon reasonable request.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr. 2019.03.007.

ACKNOWLEDGMENTS

This work was supported financially by the National Natural Science Foundation of China (21832002, 21872050, 21808063, and 91545103), the Science and Technology Commission of Shanghai Municipality (2018SHZDZX03), the Programme of Introducing Talents of Discipline to Universities (B16017) in China, the Fundamental Research Funds for the Central Universities (222201718003), and the University of Manchester, Royal Society, and Engineering and Physical Sciences Research Council (EP/P011632/1) in the UK. We are especially grateful to the Science and Technology Facilities Council (STFC) and the ISIS Neutron Facility for access to the Beamline TOSCA. We thank S. Xu, Q. Xia, C. Goodway, and M. Kibble for their help at the beamline. Computing resources (time on the SCARF cluster for the CASTEP calculations) were provided by STFC's e-Science facility.

AUTHOR CONTRIBUTIONS

L.D., X.L., and Y.G. conducted catalytic reactions and material characterizations. L.L., X.H., S.R., and S.F.P. contributed to the collection and analysis of INS data and DFT calculations. X.S. and F.L. collected and analyzed 2D-HSQC-NMR data. Y.G., S.Y., and Y.W. guided the direction of the project and contributed to the preparation of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: October 28, 2018 Revised: December 4, 2018 Accepted: March 14, 2019 Published: April 11, 2019

Chem

REFERENCES AND NOTES

- Zakzeski, J., Bruijnincx, P.C.A., Jongerius, A.L., and Weckhuysen, B.M. (2010). The catalytic valorization of lignin for the production of renewable chemicals. Chem. Rev. 110, 3552– 3599.
- Li, C., Zhao, X., Wang, A., Huber, G.W., and Zhang, T. (2015). Catalytic transformation of lignin for the production of chemicals and fuels. Chem. Rev. 115, 11559–11624.
- Ragauskas, A.J., Beckham, G.T., Biddy, M.J., Chandra, R., Chen, F., Davis, M.F., Davison, B.H., Dixon, R.A., Gilna, P., Keller, M., et al. (2014). Lignin valorization: improving lignin processing in the biorefinery. Science 344, 1246843.
- Schutyser, W., Renders, T., Van den Bosch, S.V., Koelewijn, S.F., Beckham, G.T., and Sels, B.F. (2018). Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. Chem. Soc. Rev. 47, 852–908.
- Xu, C.P., Arancon, R.A.D., Labidi, J., and Luque, R. (2014). Lignin depolymerisation strategies: towards valuable chemicals and fuels. Chem. Soc. Rev. 43, 7485–7500.
- Rinaldi, R., Jastrzebski, R., Clough, M.T., Ralph, J., Kennema, M., Bruijnincx, P.C.A., and Weckhuysen, B.M. (2016). Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis. Angew. Chem. Int. Ed. 55, 8164–8215.
- Yan, N., Zhao, C., Dyson, P.J., Wang, C., Liu, L.T., and Kou, Y. (2008). Selective degradation of wood lignin over noble-metal catalysts in a two-step process. ChemSusChem 1, 626–629.
- Rahimi, A., Ulbrich, A., Coon, J.J., and Stahl, S.S. (2014). Formic-acid-induced depolymerization of oxidized lignin to aromatics. Nature 515, 249–252.
- Wu, X., Fan, X., Xie, S., Lin, J., Cheng, J., Zhang, Q., Chen, L., and Wang, Y. (2018). Solar energydriven lignin-first approach to full utilization of lignocellulosic biomass under mild conditions. Nat. Catal. 1, 772–780.
- Sun, Z., Bottari, G., Afanasenko, A., Stuart, M.C.A., Deuss, P.J., Fridrich, B., and Barta, K. (2018). Complete lignocellulose conversion with integrated catalyst recycling yielding valuable aromatics and fuels. Nat. Catal. 1, 82–92.
- Deuss, P.J., Scott, M., Tran, F., Westwood, N.J., de Vries, J.G., and Batra, K. (2015). Aromatic monocyclics by in situ conversion of reactive intermediates in the acid-catalyzed depolymerization of lignin. J. Am. Chem. Soc. 137, 7456–7467.
- Lahive, C.W., Deuss, P.J., Lancefield, C.S., Sun, Z., Cordes, D.B., Young, C.M., Tran, F., Slawin, A.M.Z., de Vries, J.G., Kamer, P.C.J., et al. (2016). Advanced model compounds for understanding acid-catalyzed lignin depolymerization: identification of renewable aromatics and a lignin-derived solvent. J. Am. Chem. Soc. 138, 8900–8911.
- Stärk, K., Taccardi, N., Bösmann, A., and Wasserscheid, P. (2010). Oxidative depolymerization of lignin in ionic liquids. ChemSusChem 3, 719–723.

- Li, Y.D., Shuai, L., Kim, H., Motagamwala, A.H., Mobley, J.K., Yue, F., Tobimatsu, Y., Havkin-Frenkel, D., Chen, F., Dixon, R.A., et al. (2018). An "ideal lignin" facilitates full biomass utilization. Sci. Adv. 4, eaau2968.
- Rahimi, A., Azarpira, A., Kim, H., Ralph, J., and Stahl, S.S. (2013). Chemoselective metal-free aerobic alcohol oxidation in lignin. J. Am. Chem. Soc. 135, 6415–6418.
- 16. Parsell, T., Yohe, S., Degenstein, J., Jarrell, T., Klein, I., Gencer, E., Hewetson, B., Hurt, M., Kim, J.I., Choudhari, H., et al. (2015). A synergistic biorefinery based on catalytic conversion of lignin prior to cellulose starting from lignocellulosic biomass. Green Chem. 17, 1492–1499.
- Klein, I., Saha, B., and Abu-Omar, M.M. (2015). Lignin depolymerization over Ni/C catalyst in methanol, a continuation: effect of substrate and catalyst loading. Catal. Sci. Technol. 5, 3242–3245.
- Matson, T.D., Barta, K., Iretskii, A.V., and Ford, P.C. (2011). One-pot catalytic conversion of cellulose and of woody biomass solids to liquid fuels. J. Am. Chem. Soc. 133, 14090–14097.
- Song, Q., Wang, F., Cai, J., Wang, Y., Zhang, J., Yu, W., and Xu, J. (2013). Lignin depolymerization (LDP) in alcohol over nickelbased catalysts via a fragmentation– hydrogenolysis process. Energy Environ. Sci. 6, 994–1007.
- Wang, X., and Rinaldi, R. (2013). A route for lignin and bio-oil conversion: dehydroxylation of phenols into arenes by catalytic tandem reactions. Angew. Chem. Int. Ed. 52, 11499– 11503.
- 21. Van den Bosch, S., Schutyser, W., Vanholme, R., Driessen, T., Koelewijn, S.-F., Renders, T., De Meester, B., Huijgen, W.J.J., Dehaen, W., Courtin, C.M., et al. (2015). Reductive lignocellulose fractionation into soluble ligninderived phenolic monomers and dimers and processable carbohydrate pulps. Energy Environ. Sci. 8, 1748–1763.
- 22. Van den Bosch, S., Renders, T., Kennis, S., Koelewijn, S.-F., Van den Bossche, G., Vangeel, T., Deneyer, A., Depuydt, D., Courtin, C.M., Thevelein, J.M., et al. (2017). Integrating lignin valorization and bio-ethanol production: on the role of Ni-Al₂O₃ catalyst pellets during ligninfirst fractionation. Green Chem. 19, 3313–3326.
- 23. Shuai, L., Amiri, M.T., Questell-Santiago, Y.M., Héroguel, F., Li, Y., Kim, H., Meilan, R., Chapple, C., Ralph, J., and Luterbacher, J.S. (2016). Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization. Science 354, 329–333.
- Lan, W., Amiri, M.T., Hunston, C.M., and Luterbacher, J.S. (2018). Protection group effects during α, γ-diol lignin stabilization promote high-selectivity monomer production. Angew. Chem. Int. Ed. 57, 1356– 1360.
- Shuai, L., Sitison, J., Sadula, S., Ding, J., Thies, M.C., and Saha, B. (2018). Selective C-C bond cleavage of methylene-linked

lignin models and Kraft lignin. ACS Catal. 8, 6507–6512.

CelPress

- Ma, Z., Troussard, E., and van Bokhoven, J.A. (2012). Controlling the selectivity to chemicals from lignin via catalytic fast pyrolysis. Appl. Catal. A Gen. 423–424, 130–136.
- Jan, O., Marchand, R., Anjos, L.C.A., Seufitelli, G.V.S., Nikolla, E., and Resende, F.L.P. (2015). Hydropyrolysis of lignin using Pd/HZSM-5. Energy Fuels 29, 1793–1800.
- Mu, W., Ben, H., Ragauskas, A., and Deng, Y. (2013). Lignin pyrolysis components and upgrading—technology review. Bioenergy Res. 6, 1183–1204.
- Li, X., Su, L., Wang, Y., Yu, Y., Wang, C., Li, X., and Wang, Z. (2012). Catalytic fast pyrolysis of Kraft lignin with HZSM-5 zeolite for producing aromatic hydrocarbons. Front. Environ. Sci. Eng. 6, 295–303.
- Zhao, Y., Deng, L., Liao, B., Fu, Y., and Guo, Q.-X. (2010). Aromatics production via catalytic pyrolysis of pyrolytic lignins from bio-oil. Energy Fuels 24, 5735–5740.
- Vermeiren, W., and Gilson, J.-P. (2009). Impact of zeolites on the petroleum and petrochemical industry. Top. Catal. 52, 1131– 1161.
- Zhu, J., Meng, X., and Xiao, F.S. (2013). Mesoporous zeolites as efficient catalysts for oil refining and natural gas conversion. Front. Chem. Sci. Eng. 7, 233–248.
- Michaud, P., Lemberton, J.L., and Pérot, G. (1998). Hydrodesulfurization of dibenzothiophene and 4,6dimethyldibenzothiophene: effect of an acid component on the activity of a sulfided NiMo on alumina catalyst. Appl. Catal. A Gen. 169, 343–353.
- 34. Zhang, D., Duan, A., Zhao, Z., and Xu, C. (2010). Synthesis, characterization, and catalytic performance of NiMo catalysts supported on hierarchically porous beta-KIT-6 material in the hydrodesulfurization of dibenzothiophene. J. Catal. 274, 273–286.
- 35. Shao, Y., Xia, Q., Dong, L., Liu, X., Han, X., Parker, S.F., Cheng, Y., Daemen, L.L., Ramirez-Cuesta, A.J., Yang, S., et al. (2017). Selective production of arenes via direct lignin upgrading over a niobium-based catalyst. Nat. Commun. 8, 16104.
- 36. Xia, Q., Chen, Z., Shao, Y., Gong, X., Wang, H., Liu, X., Parker, S.F., Han, X., Yang, S., and Wang, Y. (2016). Direct hydrodeoxygenation of raw woody biomass into liquid alkanes. Nat. Commun. 7, 11162.
- Li, Y., Akiyama, T., Yokoyama, T., and Matsumoto, Y. (2016). NMR assignment for diaryl ether structures (4-O-5 structures) in pine wood lignin. Biomacromolecules 17, 1921– 1929.
- Ma, R., Zhang, X., Wang, Y., and Zhang, X. (2018). New insights toward quantitative relationships between lignin reactivity to monomers and their structural characteristics. ChemSusChem 11, 2146–2155.

Chem



- Yamamura, M., Hattori, T., Suzuki, S., Shibata, D., and Umezawa, T. (2010).
 Microscale alkaline nitrobenzene oxidation method for high-throughput determination of lignin aromatic components. Plant Biotechnol. 27, 305–310.
- Chui, M., Metzker, G., Bernt, C.M., Tran, A.T., Burtoloso, A.C.B., and Ford, P.C. (2017). Probing the lignin disassembly pathways with modified catalysts based on Cu-doped porous metal oxides. ACS Sustain. Chem. Eng. 5, 3158–3169.
- 41. Miyazawa, T., Kusunoki, Y., Kunimori, K., and Tomishige, K. (2006). Glycerol conversion in the

aqueous solution under hydrogen over Ru/C + an ion-exchange resin and its reaction mechanism. J. Catal. 240, 213–221.

- 42. Fihri, A., Bouhrara, M., Patil, U., Cha, D., Saih, Y., and Polshettiwar, V. (2012). Fibrous nanosilica supported ruthenium (KCC-1/Ru): a sustainable catalyst for the hydrogenolysis of alkanes with good catalytic activity and lifetime. ACS Catal. 2, 1425–1431.
- Palkovits, R., Tajvidi, K., Procelewska, J., Rinaldi, R., and Ruppert, A. (2010). Hydrogenolysis of cellulose combining mineral acids and hydrogenation catalysts. Green Chem. 12, 972–978.
- Rahimi, N., and Karimzadeh, R. (2011). Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: a review. Appl. Catal. A Gen. 398, 1–17.
- 45. Solcà, N., and Dopfer, O. (2002). Protonated benzene: IR spectrum and structure of $C_6H_7^+$. Angew. Chem. Int. Ed. 41, 3628–3631.
- 46. Parker, S.F., Fernandez-Alonso, F., Ramirez-Cuesta, A.J., Tomkinson, J., Rudic, S., Pinna, R.S., Gorini, G., and Fernández Castañon, J. (2014). Recent and future developments on Tosca at ISIS. J. Phys. Conf. Ser. 554, 012003.