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Biofuels

Highly Selective Catalytic Conversion of Phenolic Bio-Oil to Alkanes**

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Bio-oil, produced by fast pyrolysis or liquefaction of biomass, is a promising second-generation renewable energy carrier. However, owing to its high oxygen content and instability, the direct use of bio-oil as a liquid fuel is currently not feasible.[1] The aqueous acidic (containing 15–30 wt% H_2O, pH 2.5) and highly oxygenated (nearly sulfur-free, ca. 30 wt% phenolic fraction) bio-oil mixture[2] would be a very promising basic resource, if suitable catalytic technology existed for its conversion to alkanes.

Hydrodeoxygenation is considered to be the most effective method for bio-oil upgrading.[3] Conventional (sulfide-based) hydrotreating catalysts, however, contaminate products by incorporation of sulfur, deactivate rapidly by coke deposition, and are potentially poisoned by trace amounts of water.[4] Therefore, conceptually the reductive upgrading of bio-oil in an acidic aqueous medium using metal catalysts offers a new attractive alternative route. Environmentally benign water-based systems are also advantageous for the separation of the products, such as water-insoluble alkanes, from the aqueous phase.

Recently it has been reported that water is a good medium for the selective hydrogenation or oxidation of some bio-derived compounds such as polyols,[5] limonene,[6] and alcohols[7] under mild conditions and even for catalyzing the Fischer–Tropsch synthesis.[8] Herein, we report on a new catalytic route with a bifunctional combination of a stable carbon-supported noble-metal catalyst and a mineral acid to convert phenolic bio-oil components (phenols, guaiacols, and syringols) with high selectivity to cycloalkanes and methanol.

Phenol was selected as the model compound to explore the principal hydrogenation and deoxygenation routes.[9] Figure 1 a plots the conversion of phenol at 353 K with Pd/C as catalysts in the neutral aqueous solution versus reaction time. The reaction progress was accompanied by an increase in cyclohexanol selectivity and a decrease in cyclohexanone selectivity. This suggests that phenol is hydrogenated to cyclohexanone in the first step. Cyclohexanone may appear as an intermediate in the isomerization of the partial-hydrogenation product cyclohexenol. Phenol did not undergo direct hydrogenolysis to benzene. Thus, Pd as well as Pt-, Ru-, and Rh-based catalysts favor phenol hydrogenation to cyclohexanol. Exploring the catalytic chemistry in the transformation of cyclohexanol to cyclohexane (see Table S1 in the Supporting Information), we found that cyclohexanol is very stable at temperatures from 373 K to 453 K in aqueous solutions acidified with H_3PO_4, and a conversion of merely 8.6% is obtained at 453 K. However, with a further small temperature increase to 473 K, cyclohexanol was quantitatively dehydrated to cyclohexene with mineral acids within a short time.

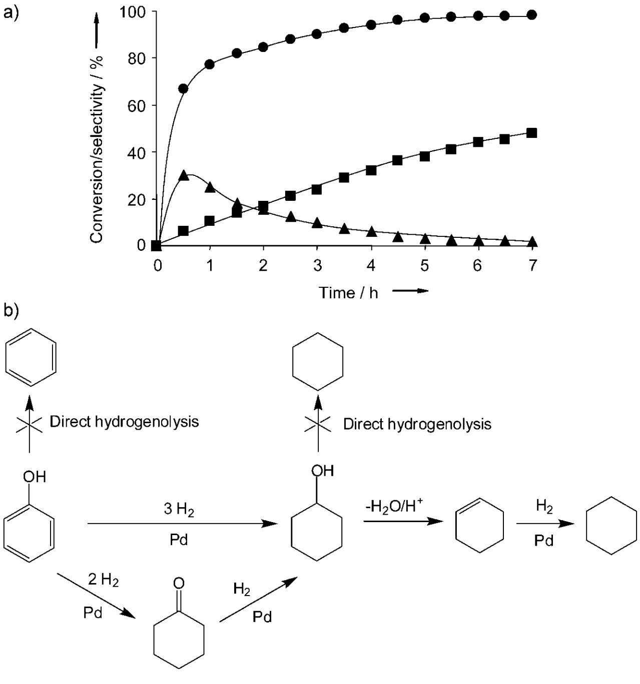

Figure 1. a) Plot of phenol conversion (■), cyclohexanol selectivity (●), and cyclohexanone selectivity (▲) for the aqueous-phase hydrogenation of phenol as a function of reaction time. Reaction conditions: phenol (1.00 g, 0.0106 mol), 5 wt% Pd/C (0.020 g, 1.04×10^{-5} mol Pd), H_2O (80 mL), 353 K, 5 MPa H_2,; reaction mixture stirred at 1000 rpm. b) Proposed reaction pathway for the aqueous-phase hydrodeoxygenation of phenol over Pd/C in the presence of an acid to give cyclohexane.

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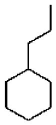
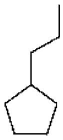
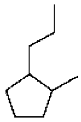
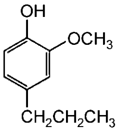
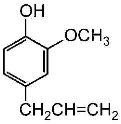
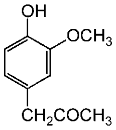
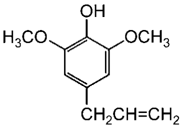
The hydrogenation of cyclohexene to cyclohexane proceeds quantitatively at high rates catalyzed by Pd-based catalysts. This implies that the formation of cyclohexane from phenol requires bifunctional catalysis, i.e., the presence of hydronium ions for dehydration at a proper temperature and a metallic function able to hydrogenate in the presence of water. The overall reaction pathway for the aqueous-phase hydrodeoxygenation of phenol to cyclohexane proceeds by an initial metal-catalyzed hydrogenation of the aromatic ring followed by acid-catalyzed dehydration of cyclohexanol and metal-catalyzed hydrogenation of the cycloalkene (Figure 1 b). Besides Pd/C, other supported noble-metal catalysts such as Pt/C, Ru/C, and Rh/C can efficiently catalyze the aqueous-phase hydrodeoxygenation of phenol to cyclohexane at 473 K in the presence of phosphoric acid, with a high yield (ca. 90 %) and a high average turnover frequency (TOF > 1200 h^{-1}; see Table S2 in the Supporting Information). The yields of cyclohexane achieved are far better than those achieved with the most active CoMo sulfide catalysts, which produced 33.8 % benzene and 3.6 % cyclohexane from phenol at 673 K in a fixed-bed reactor.[10]

Apart from phenol, more complex aromatic monomers were also successfully converted. These monomers include guaiacols and syringols, which are the most abundant aromatic compounds originating from lignin in biomass pyrolysis. Hydrogenation of these molecules leads to a large variety of products including cycloalcohols, cycloketones, arenes, cycloalkanes, and methanol. The guaiacols, including 4-*n*-propylguaiacol, 4-allylguaiacol, and 4-acetonylguaiacol (Table 1), were transformed to cycloalkanes and methanol under the conditions (523 K, 5 MPa H_2, 0.5 h). Conversion of guaiacols led to yields of approximately 80 % cycloalkanes, 7–8 % methanol, and roughly 12–18 % intermediate cycloalcohols or cycloketones, emphasizing the importance of this route in terms of energy efficiency and atom economy. Additionally, hydrogenolysis also proceeded to a low extent, forming alkanes with shorter carbon chains, for example *n*-propylcyclopentane (C8 alkanes) from 2-methoxy-4-*n*-propylphenol (C9 backbone phenol). Different *para*-substituted chains on the aromatic ring did not affect the conversion rates, even in the case of the chains carrying the acetonyl group. Syringol-like 4-allyl-2,6-dimethoxylphenol was also tested under the same conditions; 92 % conversion was achieved with a selectivity of 67 % alkanes and 12 % methanol. These results suggest that the new approach can be effectively applied for the hydrodeoxygenation of diverse substituted phenolic monomers in upgrading bio-oil phenolic components.

Additionally, it is also possible to convert complex phenolic mixtures without loss of efficiency. Phenolic monomers including 4-*n*-propylphenol, 2-methoxy-4-*n*-propylphenol, 4-hydroxy-3-methoxyphenylacetone, and 4-allyl-2,6-dimethoxyphenol were mixed in equimolar amounts to simulate a bio-oil mixture. As expected, the surrogate bio-oil was effectively hydrodeoxygenated under the reaction conditions (523 K, 5 MPa H_2, 0.5 h), maintaining a high average TOF (> 1000 h^{-1}). The conversions of the above-mentioned components range from 82 % to 100 % with selectivities of 70.2 % alkanes and 8.0 % methanol. This result is highly important as phenolic mixtures tend to polymerize; this is frequently observed in the partial deconstruction of lignin.

Table 1: Aqueous-phase hydrodeoxygenation of bio-derived aromatic monomers found in bio-oil on Pd/C catalysts with acids at 523 K.[a]

Reactant	Conv. [%]	Selectivity [%]				
					CH_3OH	Cyclic alcohol (ketone)
	100	66	3.0	6.7	7.2	17
	99	65	3.5	5.0	7.4	18
	100	71	3.1	5.2	8.2	12
	92	58	3.6	5.4	12	21

[a] Reaction conditions: reactant (0.0106 mol), 5 wt % Pd/C (0.040 g, 2.08×10^{-5} mol Pd), 0.5 wt % H_3PO_4/H_2O (80 mL), 5 MPa H_2, 0.5 h; reaction mixture stirred at 1000 rpm.

To test for catalyst recyclability, a batch of Pd/C catalyst was used repeatedly for the reaction of the substitute bio-oil mixture at 523 K and 5 MPa H_2 for 2 h. The first run reached conversions of nearly 100 % and selectivities of 89 % alkanes and 9.0 % methanol after 2 h. The GC–MS product distribution (see Figure S1 in the Supporting Information) demonstrates that phenolic monomers were quantitatively converted to cycloalkanes and methanol. Nearly quantitative conversions and very high selectivities (roughly 80 % alkanes and 8 % methanol) were also obtained in two subsequent experiments with recycled catalysts.

To explore the reaction pathway of the hydrodeoxygenation of phenol derivatives, guaiacol, whose aromatic ring has adjacent methoxy and hydroxy functional groups, was hydrotreated at the low temperature of 423 K with Pd/C and H_3PO_4 as catalysts (see Figure 2 a). The main initial product, 2-methoxycyclohexanone, was gradually hydrogenated to 2-methoxycyclohexanol, suggesting that the fastest step is the metal-catalyzed hydrogenation of the aromatic ring and not the hydrolysis of the methoxy group. As methoxycyclohexanol can be readily hydrolyzed and dehydrated in the presence of hydronium ions and Pd/C at 523 K in a short time to cyclohexanone and methanol, we speculate that the primary reaction pathway for methoxycyclohexanol conver-

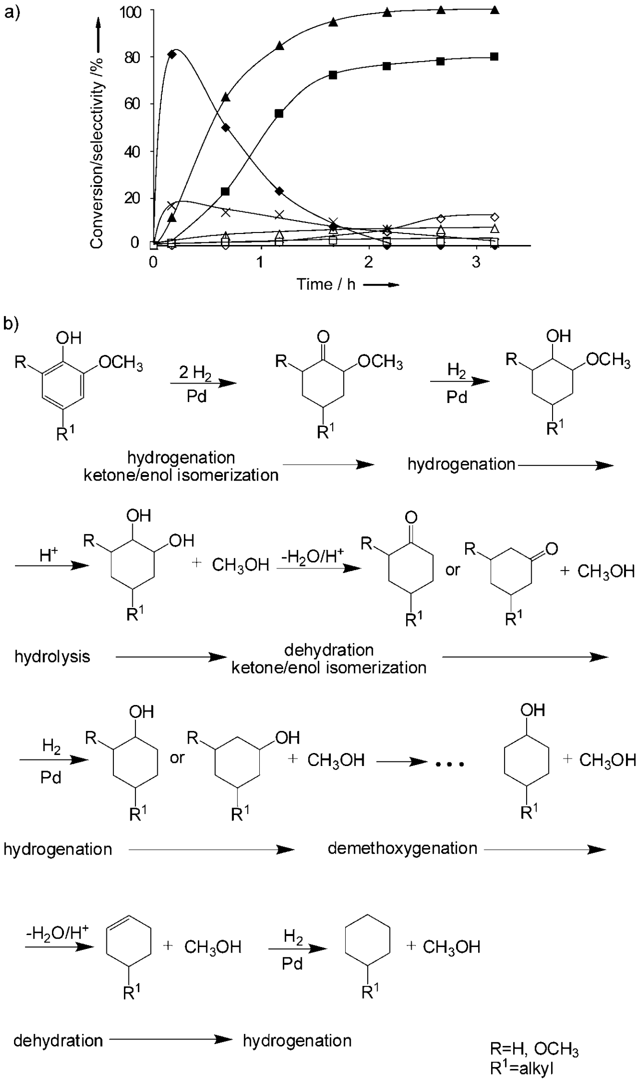


Figure 2. a) Product distribution after the hydrogenation of guaiacol at 423 K with H^+ over Pd/C as a function of time: guaiacol conversion (▲), 2-methoxycyclohexanol selectivity (■), 2-methoxycyclohexanone selectivity (◆), cyclohexanol selectivity (◇), cyclohexanone selectivity (×), methoxyhexane selectivity (△), 2-hydroxycyclohexanone selectivity (+), methanol selectivity (□). Reaction conditions: guaiacol (1.314 g, 0.0106 mol), 5 wt% Pd/C (0.020 g, 1.04×10^{-5} mol Pd), 0.5 wt% H_3PO_4/H_2O (80 mL), 5 MPa H_2; reaction mixture was stirred at 1000 rpm. b) Proposed reaction pathway for aqueous-phase hydrodeoxygenation of phenolic aromatics to alkanes and methanol over a metal catalyst and with an acid.

sion is the acid-catalyzed hydrolysis to methanol and 1,2-cyclohexanediol followed by the (acid-catalyzed) dehydration of the latter product to cyclohexanone. Cyclohexanone is in turn gradually converted to cyclohexanol. Combined with the results from dehydration of cyclohexanol (see Table S1 in the Supporting Information), we propose the general pathway in Figure 2b for the conversion of aromatic monomers to alkanes. Under appropriate conditions, aromatic monomers such as guaiacol, are first hydrogenated at the aromatic ring to give 2-methoxycyclohexanone and subsequently 2-methoxycycloalcohol. The reaction sequence continues with the acid-catalyzed ether hydrolysis to form the cyclodiol and dehydration of the diol to give the cycloketone. The sequential hydrogenation of the cycloketone leads to the cycloalcohol. Acid-catalyzed alcohol dehydration and metal-catalyzed cycloalkene hydrogenation lead to the target cycloalkane. This reaction pathway for the stepwise aqueous-phase hydrodeoxygenation of phenolic monomers is based on bifunctional catalysis, that is, coupling metal-catalyzed hydrogenation and acid-catalyzed hydrolysis and dehydration; this pathway differs drastically from that of C–O bond hydrogenolysis with sulfide catalysts.[1,11]

In conclusion, a new and efficient catalytic route for the production of alkanes by upgrading the aqueous phenolic bio-oil has been developed. A carbon-supported noble-metal catalyst in combination with the mineral acid H_3PO_4 act as bifunctional catalysts for the one-pot hydrodeoxygenation conversion of bio-oil through the multistep reactions consisting of hydrogenation, hydrolysis, and dehydration. The mixture of alkane products forms a second phase, which can be easily separated from the aqueous phase. The new route provides a feasible approach for the direct use of crude aqueous bio-oil mixture, facilitating an energy-efficient and atom-economic process.

Experimental Section

The carbon-supported palladium catalysts were obtained from Aldrich. In a typical test, phenol (1.00 g, 0.0106 mol) or monomer (0.0106 mol), 0.5 wt% H_3PO_4/H_2O (80 mL), and 5 wt% Pd/C (0.040 g, 2.08×10^{-5} mol Pd) were added to a Parr reactor (reactor volume, 300 mL). After purging the reactor with H_2, the reaction was carried out with 5 MPa H_2 (room temperature) at 473 K or 523 K for 0.5 h at a stirring speed of 1000 rpm. After the reaction was halted, the reactor was cooled to room temperature. Ethyl acetate was used to extract the organic mixture, and the aqueous phase was also collected. The aqueous and organic layers were both analyzed by GC and GC–MS. Internal standards (i.e., 2-isopropylphenol for the organic phase and acetone for the aqueous phase) were used to determine the product amount and carbon balance. The gas-phase products were analyzed by GC. Conversion = (amount of non-aromatic products/total amount of aromatic compounds in the starting material) × 100%. Selectivity = (C atoms in each product/total C atoms in the products) × 100%; Carbon balance is better than $95\pm3\%$ in this work.

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