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Article

Single-step conversion of lignin monomers to phenol: Bridging the gap between lignin and high-value chemicals

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ABSTRACT

Transformation of lignin into high-value chemicals is hampered by the complexity of monomers obtained from lignin depolymerization. Here we report a strategy, composed of hydro-demethoxylation and de-alkylation reactions, that is able to chemically converge various lignin-derived phenolic monomers into phenol in a single-step. Using 2-methoxy-4-propylphenol as a model compound, Pt/C exhibited the best performance in hydro-demethoxylation reaction affording >80% 4-propylphenol from 2-methoxy-4-propylphenol, while H-ZSM-5 was identified as the most suitable catalyst for de-alkylation, achieving 83% yield of phenol from 4-propylphenol. Since the two catalysts operate under compatible conditions, combining the two catalysts to simultaneously promote both hydro-demethoxylation and de-alkylation reactions was achieved. Configuration of how to organize the catalysts is a critical parameter, where the physical mixture of the two was most effective, providing over 60% phenol from 2-methoxy-4-propylphenol in a single-step.

1. Introduction

Lignin, a main component of lignocellulosic biomass accounting for 15%–30% by weight and 40% by energy [1,2], is still not sufficiently used in biorefineries. Despite the significant advances in lignin depolymerisation via hydrogenolysis [3–21], oxidation [22–27], hydrolysis [28–34], thermal [35–37], photo- [38–40] and electro-chemical [41] transformations in the past decade, the depolymerized lignin is most often a complex mixture of phenolic compounds hampering direct use as high-value chemicals. This is first of all attributed to the non-uniform nature of lignin. Unlike cellulose [42] and chitin [43], the top two biopolymers in nature—that contain only one monomer linking together primarily by 1,4-glycosidic bond in a liner form, lignin is composed of three types of substituted phenols connected by a number of C–O and C–C bonds, forming a three-dimensional amorphous, irregular polymer. Second, lignin polymers may undergo non-selective fragmentation and rearrangement during depolymerisation [13], further complicating the product stream.

One solution to the problem is to produce lignin with a simpler structure via generic engineering. For instance, overexpression of the ferulate 5-hydroxylase gene in poplar (Populus spp.) affords lignin with almost pure syringyl units and close to 90% β-O-4 linkages [4]. Nevertheless, this technique is currently not widely applied and its economic viability remains to be seen. Another solution is to develop strategies that are able to converge complex monomers derived from lignin into a sin-

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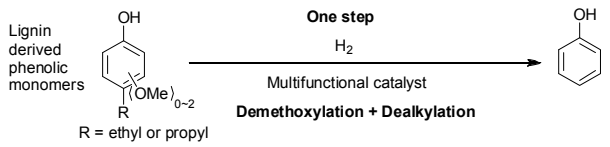
gle stream. An elegant biological funnelling strategy was proposed and developed, in which a lignin liquor stream was converted to polyhydroxyl acid, forming the foundation of various end uses [44]. As far as we are aware, one-step chemical transformation that convert, or conceptually that are able to convert, lignin derived monomer mixtures such as 2-methoxy-4-propylphenol and 2,6-dimethoxy-4-propylphenol into a single value-added product is very rare.

Despite the complexity of decomposed lignin, the structures of the products are not without patterns. A common feature for the monomers obtained from lignin under neutral or reductive conditions is that they are substituted phenols bearing zero to two methoxyl groups in the *ortho*-position and an alkyl group in the *para*-position. If highly selective de-methoxyl [45–53] and de-alkyl [54–61] chemistry could simultaneously occur, one may anticipate that a mixture of substituted phenols to be converted into a single-compound phenol (Scheme 1). Notably, phenol is one of the most important aromatic chemicals utilized in industry reaching an annual production of 8.9 million tons [51], mainly used as synthetic polymer precursors such as bisphenol-A and nylon [62,63], as well as pharmaceuticals and herbicides. Its current production is mainly through the Hock Process based on petroleum feedstock, including oxidation of cumene with oxygen and then cleavage of the cumene peroxide formed in the first step to afford phenol and acetone in a 1:1 ratio [62]. One disadvantage of the process, among others, is that the demand for phenol far exceeds the demand for acetone. Previously, converting alkyl phenols into phenol has been reported, but the substrates are limited to non-methoxyl group containing ones [54–58].

In this work, we developed a single-step route to convert lignin derived monomers into phenol using 2-methoxy-4-propylphenol as a model compound. To identify proper catalyst combination, we first optimized 2-methoxy-4-propylphenol conversion into 4-propylphenol over noble metal catalysts in the presence of hydrogen. Then de-alkylation of 4-propylphenol into phenol was evaluated and optimized using zeolite catalysts. We further demonstrated a single-step protocol to convert 2-methoxy-4-propylphenol into phenol, by physical mixing Pt/C and H-ZSM-5 catalysts. Catalyst screening, reaction condition optimization, effect of water, as well as the effect of the way to mix the two catalysts in single-step conversion were studied. We also studied the deactivation mechanism for de-alkylation, and propose possible ways to regenerate the catalysts.

2. Experimental

Technical grade H_2 (99.99%), forming gas (20% H_2), nitrogen (99.99%), air (21% ± 1% O_2), CO (99.8%) were acquired from Air Liquide. 2-methoxy-4-propylphenol (≥99%), 4-propylguaiacol (≥99%), 4-propylphenol (≥97%), platinum on carbon (5 wt%), platinum on silica (1 wt%), platinum on alumina (5 wt%), palladium on carbon (10 wt%) were purchased from Sigma-Aldrich. H-ZSM-5 (SiO_2/Al_2O_3 = 25), HUSY (SiO_2/Al_2O_3 = 14), and beta zeolite (SiO_2/Al_2O_3 = 25) were obtained from the Catalyst Plant of Nankai University. Dichloromethane (HPLC grade) and ethanol (HPLC grade) were from VWR Chemicals. Multiwall carbon nanotubes (MWCNT) (ø: 20–40 nm; 70–120 m^2/g) were purchased from Shenzhen Nanotech Port Co., Ltd. $Pt_1/m\text{-}Al_2O_3$ [64], 5 wt% Pt/MWCNT [65] and Mn-P-ZSM-5 [55] were prepared following literature methods. In the above, Pt_1 refers to the single-atom identify of Pt species, whereas $m\text{-}Al_2O_3$ stands for mesoporous alumina [64].



Scheme 1. The strategy to truncate lignin derived phenolic monomers to phenol, together with methanol and alkenes as valuable side-products.

2.1. Hydro-demethoxylation

In a typical experiment, 2-methoxy-4-propylphenol was injected at a defined flow rate by a syringe pump (Harvard Appartus, PHD 2000 Infusion, or LongerPump, LSP04-1A) into a stainless steel reactor tube (outer diameter of 10 mm) containing the catalyst. The catalyst was fixed in the middle of the reactor tube using silica wool. Hydrogen gas or a mixture of hydrogen/nitrogen gas was delivered to the tubular reactor at a precise flow rate by using a mass flow controller. The liquid products were trapped by bubbling through ice-water cooled DCM (25 mL), and then analyzed by GC-FID and GC-MS techniques. The reactant conversion and product yield were determined using dodecane as an internal standard. Several catalysts were tested under different reaction conditions by changing the temperature, the gas composition, gas and substrate flow rate, as well as catalyst amount.

2.2. De-alkylation

For the de-alkylation of propylphenol, the same stainless steel tubular reactor as the hydro-demethoxylation reaction was employed. Zeolite catalysts were tested and placed in the middle of the furnace. Substrate and water were fed by using two syringe pumps (Harvard Appartus, PHD 2000 Infusion, and LongerPump, LSP04-1A). A mass flow controller was again used to control the flow rate of the gas (hydrogen/nitrogen mixture with 20% hydrogen, nitrogen or purified hydrogen). Products were trapped by bubbling through ice-water cooled DCM (25 mL) and analyzed by GC-FID or GC-MS using dodecane as an internal standard.

2.3. Combined hydro-demethoxylation and de-alkylation reactions

Combined reactions were conducted in a similar manner as that described for hydro-demethoxylation and de-alkylation reactions. The major difference is that the two catalysts were mixed using different configurations inside the reactor, as provided in Section 3.3.