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## **Efficient Conversion of Pine Wood Lignin to Phenol**

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**Abstract:** Obtaining chemical building blocks from biomass is attractive in order to meet sustainability targets. Herein we report an effective approach to convert the lignin part of woody biomass into phenol, which is valuable base chemical. Monomeric alkylmethoxyphenols are obtained from pinewood, rich in guaiacol-type lignin, through Pt/C-catalyzed reductive depolymerization. In a second step an optimized MoP/SiO<sub>2</sub> catalyst is used to selectively remove methoxy groups in these lignin monomers to generate 4-alkylphenols, which are dealkylated by a zeolite-catalyzed transalkylation to a benzene stream. The overall yield of phenol based on the initial lignin content in pinewood is 9.6 mol%.

Lignocellulosic biomass holds great promise as a source of sustainable chemicals replacing fossil resources. Lignin is the largest renewable source of aromatics, which explains the substantial interest from the chemical industry.<sup>[1]</sup> Many different methods have already been explored to depolymerize the recalcitrant polyphenolic network of lignin into aromatic monomers.<sup>[2]</sup> Among these, the lignin-first process (LFP) stands out in terms of the high yield of monomers, in the form of alkylmethoxyphenols, using optimized catalysts to cleave the linkages that bind lignin fragments to hemicellulose and lignin intralinkages.<sup>[3]</sup> As the market demand for these alkylmethoxyphenols represents a small size, it is desirable to convert them into bulk chemical building blocks.<sup>[4]</sup> For instance, Song et al. described an approach to convert 2-methoxy-4propylphenol to teraphthalic acid through demethoxylation, carbonylation and oxidation.<sup>[5]</sup> Other than terapthalic acid, the removal of the methoxy functionalities and alkyl side groups can give access to phenol, which is a valuable intermediate in the manufacture of agro-chemicals, detergents, plastics, medicine, dyes and plasticizers.<sup>[6]</sup> We earlier explored a combination of hydrodemethoxylation (HDMeO) and transalkylation of the alkyl groups to a benzene co-reactant in order to obtain phenol from the same lignin model compound in a one-step approach.<sup>[7]</sup> Full conversion of 2-methoxy-4-propylphenol, representative for guaiacol-type alkylmethoxylphenols obtained from LFP, was achieved with a reasonable phenol yield of 60%. The bifunctional catalytic approach combined hydrodemethoxylation catalysed by Au/TiO2 and transalkylation of the propyl side group to benzene using a zeolite catalyst. The limited phenol yield is due to the low efficiency of the demethoxylation step, while the use of gold also raises concerns about the scale-up of this process.

Earth-abundant metals (e.g. Ni, Mo, Fe), which can replace noble metals, and their corresponding oxide, carbide, sulfide, phosphide compounds have been reported as potential candidates for the deoxygenation of biomass-derived molecules.<sup>[8]</sup> Among them, transition metal phosphides show promising properties in the selective removal of oxygen in ligninderived molecules without hydrogenation of the aromatic ring. For example, 80% of a gaseous guaiacol feed could be converted using a supported Ni<sub>2</sub>P catalyst with benzene (60%) and phenol (30%) as main products.<sup>[9]</sup> In this work, we explored the potential of metal phosphides in the bifunctional upgrading of 2-methoxy-4-propylphenol to phenol as a model reaction. Our approach was to first optimize the transition metal phosphide towards optimum HDMeO of 2-methoxyl-4-propylphenol to 4propylphenol. MoP/SiO<sub>2</sub> was identified as the most promising metal phosphide, because the product yield was 88 mol% without touching the aromatic ring. The optimization of this catalyst in the bifunctional conversion of 2-methoxyl-4propylphenol to phenol led to a phenol yield close to 90 mol% at 350 °C at a high weight hourly space velocity of 40 h<sup>-1</sup>. The optimized system and conditions were then applied to convert a LFP-derived lignin oil from pinewood into phenol. This strategy opens a new avenue in the valorization of biomass towards bulk chemicals, contributing to a greener chemical industry.

We first optimized the HDMeO function by comparing FeP/SiO<sub>2</sub>, CoP/SiO<sub>2</sub>, Ni<sub>2</sub>P/SiO<sub>2</sub>, WP/SiO<sub>2</sub> and MoP/SiO<sub>2</sub> using 2-methoxy-4-propylphenol as a model compound. The metal phosphides were prepared by a two-step wetness impregnation method of appropriate metal salts and diammonium hydrogen phosphate, followed by reduction at 700 °C aiming at the conversion of the metal oxide precursor to the corresponding phosphide (supporting information section 2.1). Silica is a preferred support for metal phosphides.<sup>[10]</sup> Elemental analysis confirms proper metal and phosphorus loadings and metal-to-phosphorus ratios (Table S1). The formation of metal phosphides is evidenced by XRD (Figure S1) and XPS (Figure S2).

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Figure 1. Conversion of 2-methoxyl-4-propyl phenol demethoxylation and product distribution over different metal phosphide catalysts: FeP/SiO<sub>2</sub>, CoP/SiO<sub>2</sub>, Ni<sub>2</sub>P/SiO<sub>2</sub>, WP/SiO<sub>2</sub>, MoP/SiO<sub>2</sub> and MoO<sub>3</sub>/SiO<sub>2</sub> catalyst. Pretreatment conditions: 100 mg of catalyst is reduced in 100 ml/min H<sub>2</sub> at 450 °C for 1 hour. Reaction conditions: 5 mol% of 2-methoxyl-4-propylphenol in benzene, 350 °C, 90 bar, gas flow rate 30 ml/min H<sub>2</sub>, weight hourly space velocity (WHSV) 80 h<sup>-1</sup>.

The reduced catalysts were used to demethoxylate 2-methoxy-4-propylphenol at 350 °C under 90 bar of H<sub>2</sub> pressure using benzene as the solvent (Figure 1).<sup>[7],[11]</sup> The desired reaction is the removal of the methoxy group from the model reactant, which yields 4-propylphenol and methanol. Removal of the phenolic hydroxyl group is more difficult and would lead to the formation of propylbenzene, while aromatic ring hydrogenation is another possible side-reaction yielding propylcyclohexane. The reactant as well as the aromatic products can also be ringalkylated by methanol. The lowest product yield is obtained with the incompletely reduced Fe-based catalyst. CoP/SiO<sub>2</sub> converts the first hour 84% of the reactant with a 45% yield of 4propylphenol, 18% of methylated 4-propylphenols and 6% of npropylbenzene. Although the product distribution is promising and aromaticity is retained, this catalyst suffers from severe deactivation. A higher and more stable conversion is attained with Ni<sub>2</sub>P/SiO<sub>2</sub> as the catalyst. However, a drawback of this catalyst is that hydroxyl group removal and aromatic ring hydrogenation proceeded at substantial rates, leading to the formation of *n*-propylcyclohexane. The higher aromatic ring hydrogenation rate also leads to hydrogenation of the solvent, which is highly undesired (Figure S3). WP/SiO<sub>2</sub> shows a reasonable 4-propylphenol yield of 40 mol% with a relatively small amount of methylated 4-propylphenols by-product. However, the conversion rate was low with this catalyst. The best performance was obtained with the MoP/SiO<sub>2</sub> catalyst, enabling a near complete conversion of 2-methoxy-4propylphenol with an 88 mol% yield of 4-propylphenol. Remarkably, this catalyst can remove the methoxy group without touching the phenolic hydroxyl group or the aromatic ring. The major by-products are methylated 4-propylphenols (10 mol%). Besides the nearly quantitative yield of alkylphenols, the catalyst also exhibited good stability during 6 h of reaction. While the desirable selectivity can be correlated to the intrinsic catalytic properties of MoP, the high activity can be related to the significantly higher dispersion of the MoP phase on silica

compared to the other catalysts as judged from CO uptake measurements (Table S1). In contrast to the other metal phosphides, TEM shows a high MoP dispersion (Figure S4). The high dispersion of MoP can be caused by the metal weight loading and the mobility of metal phase in reduction process (Table S2).<sup>[12],[13]</sup> As earlier work indicated that MoO<sub>3</sub> is also a potential catalyst for the deoxygenation of lignin monomers,<sup>[14]</sup> we compared MoP/SiO<sub>2</sub> to MoO<sub>3</sub>/SiO<sub>2</sub> in our model HDMeO reaction. Although MoO<sub>3</sub>/SiO<sub>2</sub> can also convert 2-methoxy-4-propylphenol to the desired reaction product, MoP/SiO<sub>2</sub> is much more active and produces less by-products. These results highlight the unique ability of MoP/SiO<sub>2</sub> for the selective removal of the methoxy group of 2-methoxy-4-propylphenol by HDMeO.

Obtaining phenol from the demethoxylated intermediate requires the removal of the alkyl group for which we explored transalkylation to another aromatic molecule. Zeolites are shape-selective catalysts for various kinds of alkylation/dealkylations reactions.<sup>[15]</sup> These catalysts can also be involved in transalkylation, allowing a shift from alkyl groups from one aromatic molecule to another.<sup>[16]</sup> We exploit this latter property by using benzene as a solvent, which is present in excess to the lignin monomer. In addition to the formation of valuable phenol, this approach also increases the value of the benzene stream. Alkylated benzenes are more valuable than benzene in the chemical industry. We selected acidic HZSM-5 with Si/Al 15 as a transalkylation catalyst. In a typical reaction, a mixture of 100 mg passivated MoP/SiO<sub>2</sub> (particle size 75-200 µm) and 100 mg of HZSM-5 (particle size 300-500 µm) were mixed and placed in a stainless-steel fixed-bed reactor (Figure 2a). Figure 2b (left) shows the results of catalytic tests using a feed of 2-methoxy-4-propylphenol and benzene (1:20 molar ratio) at 350 °C and 90 bar H<sub>2</sub> at WHSV 40 h<sup>-1</sup>. The combined demethoxylation by MoP/SiO2 and transalkylation by zeolite resulted in a promising phenol yield of 83% after 1 hour. The propyl chain is mainly transferred to benzene yielding npropylbenzene and cumene. These products have particular value in the current context as they can be converted to phenol by oxidation.<sup>[17]</sup> Toluene and xylenes were other reaction products, which are most likely obtained by alkylation of benzene with methanol derived from removal of the methoxy group as well as isomerization reactions of cumene and npropylbenzene. Furthermore, the observation of diphenylmethane (3 mol%) points to dimer formation, which can slowly accumulate and then result in the coke formation (Figure S5, S6). Propane (1 mol%) was found dissolved in benzene and also a minor amount of methane can be formed as the gaseous products due to the propyl guaiacol demethylation catalyzed by HZSM-5.<sup>[7]</sup> Although the initial phenol yield was high during the first hour, the catalyst deactivated as evident from the slowly decreasing phenol yield. This is clearly due to a loss of the transalkylation activity, because the 4-propylphenol yield increases with time on stream (Figure 2b left). A similar trend is observed among benzene-derived products in which the propylbenzene yield became lower with time on stream (Figure S7).

To investigate the origin of this undesired activity loss, the used HZSM-5 zeolite was separated from the catalyst mixture by sieving (different particle sizes were used for the two catalyst components) and analysis by XPS (Figure 2a). XPS shows that the used zeolite contains phosphate species as evident from the P 2p signal at 134.9 eV (Figure 2c). Importantly, the zeolite

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**Figure 2.** One-pot conversion of 2-methoxy-4-propylphenol to phenol in a fixed-bed flow reactor, separation of the two catalytic components of the used catalysts and XPS analysis of used HZSM-5 (a); conversion and product yield using HZSM-5 with passivated MoP/SiO<sub>2</sub> (left in b) and non-passivated MoP/SiO<sub>2</sub> (right in b). Pretreatment: reduction of 100 mg MoP/SiO<sub>2</sub> and 100 mg HZSM-5 at 450 °C for 1 hour. Reaction conditions: 5 mol% of 2-methoxyl-4-propyl phenol in benzene, 350 °C, 90 bar, H<sub>2</sub> flow rate 30 ml/min, weight hourly space velocity (WHSV) 40 h<sup>-1</sup>. P 2p (c) and Mo 3d (d) XPS spectra of used HZSM-5 catalyst.

component does not contain molybdenum nor other (reduced) phosphide species (Figure 2d). Thus, we can firmly conclude that unreduced phosphate left over from the preparation migrated from the MoP/SiO<sub>2</sub> component to HZSM-5 during the ongoing reaction. Although phosphate is regarded as a promoter for the hydrothermal stability of HZSM-5, it strongly interacts with Brønsted acid sites of zeolites, lowering the total acidity and thus the activity.<sup>[18]</sup> This deactivation mechanism is confirmed by the poor performance (lower conversion and phenol yield) of a phosphate-modified HZSM-5 in comparison to a P-free HZSM-5 zeolite in 4-propylphenol transalkylation (Figure S8). Thus, we can firmly conclude that the zeolite acid sites are deactivated by phosphate species migrating from the MoP/SiO<sub>2</sub> to HZSM-5. We considered that these phosphate species can originate from the passivation procedure of the MoP phase during the reduction step and possibly the further exposure in ambient air when loading the reactor. In order to verify this, we developed a protocol in which the reduced MoP/SiO2 was directly mixed with the zeolite catalyst and loaded into the reactor in a nitrogenflushed glovebox. Figure 2b (right) show that this approach yielded a more stable catalyst system for phenol production. A high and stable phenol yield of ~80% was obtained with cresol as the main by-product. The alkylation of benzene in this modified approach was also confirmed and the yield of alkylated products with time on stream was also stable (Figure S7). Thus, preventing MoP oxidation, which would otherwise generate phosphate species, is a key factor in obtaining a stable catalyst for a high phenol yield.

In recognizing the importance of avoiding phosphate, we optimized the preparation of MoP by varying the reduction temperature required to obtain the phosphide from Mo-oxide and phosphate precursors in the 600-900°C range (Figure S9-S11). The catalytic performance of these differently reduced MoP/SiO<sub>2</sub>

catalysts was evaluated in combination with HZSM-5 for the conversion of 2-methoxy-4-propylphenol to phenol. The conversion in these tests was complete and the phenol yield was very high with typical cresol yields of about 10 mol% (Figure S12). There was no observable deactivation during these measurements, as also confirmed by the near constant yield of *n*-propylbenzene and cumene (Figure S13). Despite the minor effect on the conversion, Figure 3 shows that a higher reduction temperature results in a higher phenol yield. The higher degree of MoP formation and the slightly lower amount of residual phosphate can contribute to these improvements. XPS analysis of used MoP/SiO<sub>2</sub> catalysts shows that the Mo oxidation state did not change during the reaction (Figure S14). Nevertheless, we still observed a small loss of phosphate species from the

 $(NH_4)_2HPO_4 + MoO_3 + 11/2H_2 \longrightarrow MoP + 2NH_3 + 7H_2O$ 



Figure 3. Influence of reduction temperature on phosphide formation (blue), 2methoxy-4-propylphenol conversion (black) and phenol yield (red, average yield during 6 h reaction).

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Figure 4. Schematic representation of the three-step approach developed in this work to obtain phenol from woody biomass. decrease of the corresponding XPS P 2p feature. The phosphorus content on used zeolite was very high (0.7 wt%) in the experiment in which MoP/SiO<sub>2</sub> was reduced at 600 °C and lowest in the experiment in which reduction was carried out at 900 °C (0.4 wt%) (Figure S15, S16). In summary, we developed a valorization of lignin monomers ob wood by LFP. In a relevant exconverted to phenol using a depolymerization of *in planta* l

The above results show the promise of using a combination of MoP/SiO<sub>2</sub> and HZSM-5 zeolite in converting lignin-derived guaiacol-type compounds in high yield to phenol. We also evaluated the stability of this catalyst combination in a 48 hours reaction (Table S3). The phenol yield was found to slowly decrease with time due to the coke formation in used HZSM-5. After catalyst regeneration at 700 °C for 2 hours in a hydrogen atmosphere, the phenol yield was 85% again. The utility of this catalyst combination in converting a syringol-type 2,6dimethoxy-4-propylphenol, in separate demethoxylation and transalkylation reactions showed that the phenol yield in this case was much lower at 31 mol% with a non-closed mass balance, likely due to oligomerization of intermediates (Table S4 and S5). Although further investigations are needed to more efficiently convert syringol-type intermediates coming from hardwood biomass, we decided to evaluate the potential of our approach on a real lignin oil derived from pinewood by LFP (Figure 4). We choose pinewood, because this kind of softwood is rich in guaiacol-type building blocks. For the LFP, pinewood sawdust was subjected to a reaction at 230 °C and 30 bar H<sub>2</sub> using a Pt/C catalyst in a methanol-water mixture (molar methanol-to-water ratio <sup>1</sup>/<sub>2</sub>).<sup>[19]</sup> All β-O-4 lignin interlinkages in the original biomass were cleaved as confirmed by HSQC NMR (Figure S19). Gel permeation chromatography evidenced the formation of lignin monomers with only a small amount of relatively low-molecular-weight lignin fragments being dissolved in benzene (Figure S20). The total monomer yield was 15 wt% of which 78% was 2-methoxy-4-propylphenol. Other lignin monomers were guaiacol, methylguaiacol and ethylguaiacol. The lignin monomers in this oil were then further converted by our combination of MoP/SiO2 and HZSM-5 catalysts (Figure S21). Not only 4-propylguaiacol, but also ethylguaiacol and methylguaiacol were converted to phenol, showing that our approach is broadly able to convert substituted guaiacols. Importantly, full conversion of these compounds in the lignin oil and stable phenol yield support our conclusion that the dualcatalyst is stable for at least 6 h. Based on the initial lignin content in pinewood, we determined a phenol yield of 9.6 mol%.

In summary, we developed a novel catalytic approach for valorization of lignin monomers obtainable from different types of wood by LFP. In a relevant example, lignin in pinewood is converted to phenol using a combination of reductive depolymerization of in planta lignin followed by combined hydrodemethoxylation and transalkylation. The upgrading of the carbohydrate pulp to value-added products via different strategies has already been explored before.<sup>[20]</sup> The novelty of our approach is the use of relatively cheap MoP/SiO<sub>2</sub> to catalyse hydrodemethoxylation. We demonstrated that the formation of MoP species is not only important for a high demethoxylation activity, but also essential to limit the amount of remaining phosphate precursor to stabilize the performance. A too high residual phosphate yield leads to slow deactivation of the zeolite component due to migration to Brønsted acid sites. Conceptually, an advantage of the described approach is the benefit of integrating the described novel biobased process in existing chemical processes for phenol production.

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**Keywords:** biomass • phenol • lignin-first • demethoxylation • transalkylation

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#### **Entry for the Table of Contents**



Phenol is obtained from renewable woody biomass in a promising yield through lignin reductive depolymerization, demethoxylation and transalkylation.