# Catalyst Support and Solvent Effects during Lignin Depolymerization and Hydrodeoxygenation

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**S** Supporting Information

**ABSTRACT:** We studied and compared the hydrodeoxygenation (HDO) and depolymerization of aldehyde-stabilized lignin and 4-propylguaiacol (PG), a model lignin monomer. We demonstrated by liquid phase adsorption that PG HDO catalyzed by Ru/C can be achieved in isooctane but not in 1,4-dioxane due to competitive solvent binding to the active sites. Unfortunately, alkanes cannot be used as solvents for real lignin due to limited solubility. However, we show that competitive solvent binding is suppressed when switching from activated carbon to oxophilic metal oxide supports such as TiO$_2$, yielding 32%mol of an equimolar mixture of cyclohexanes and cyclohexanols from real lignin.



**KEYWORDS:** Lignin, Hydrodeoxygenation, Depolymerization, Ruthenium
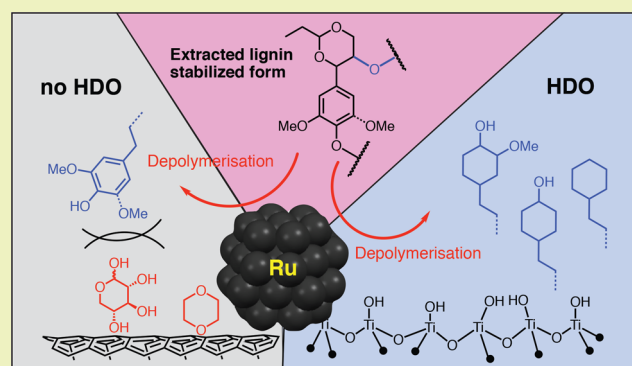
## INTRODUCTION

Lignin is the largest natural source of aromatic functionalities and, as such, is a promising source of renewable phenols or cyclic alkanes. It is one of the three main constituents of lignocellulosic biomass, along with cellulose and hemicellulose, which are two polysaccharides, and is a heteropolymer containing phenyl propane subunits linked by mostly ether bonds and some (typically 20−50%) C−C linkages. After its extraction from biomass, lignin is typically depolymerized by hydrogenolysis to produce substituted phenols such as syringols and guaiacol derivatives (Scheme 1A).[1] Since applications of these methoxylated phenyl propanoid molecules are limited, oxygen removal can be used to increase the applications of lignin-derived monomers by subsequent hydrodeoxygenation (HDO) to yield alkylated phenols, cyclohexanols, benzenes, or cyclohexanes.[2] Aromatics are sometimes more desirable products, as ring saturation increases hydrogen consumption. However, fully saturated products are sometimes valued in certain fuel applications.[3] Pt, Rh, Pd, and Ru exhibit high hydrogenolysis activity, and there is a strong selectivity dependence on metal during lignin depolymerization. For instance, contrary to Pd, Ru is able to cleave an aliphatic C−O bond as is frequently observed with model compounds.[4,5] While Pt-, Ni-, and Mo-based sulfides have been studied extensively,[6,7] Ru is frequently chosen due to its exceptional hydrogenation and hydrogenolysis activity.[8] Bifunctional materials can perform phenol HDO via ring hydrogenation on noble metal followed by dehydration−hydrogenation on an acidic support.[9] Ru/TiO$_2$ has been previously reported as an excellent catalyst for guaiacol[10] and

substituted phenol HDO.[11] In summary, HDO is frequently observed when using Ru and lignin model compounds. However, we and others have reported that no demethoxylated or other deoxygenated monomers are produced during Ru catalyzed lignin depolymerization.[1,12]

One of the reasons for the discrepancy between reactions with phenols and real lignin could be attributed to the difference in conditions between those used with model compounds and those required when using real lignin. The HDO of alkylated phenols or their methoxylated derivatives (syringols and guaiacols) is typically performed under hydrogen pressure using supported metal nanoparticles such as Ru/C, in the gas phase[2,13−16] or in the liquid phase using solvents such as alkanes,[17,18] neutral-pH water, or biphasic systems[19] to achieve reasonable levels of HDO at temperature below 300 °C. As we and others have observed, limited or no HDO activity is observed in the presence of polar organic solvents.[1,20] HDO activity can be similarly suppressed in the presence of impurities.[21] Though discussed the literature, the effects of these different conditions have not been studied in detail. Furthermore, these favorable HDO conditions greatly limit their applicability to lignin. In fact, the use of gas phase, apolar solvents or water generally limits a process's scope to model compounds, since lignins are nonvolatile and largely insoluble in apolar solvents or water. Solubility is not only essential for achieving reasonable lignin depolymerization

**Scheme 1. Steps of Combined Lignin Depolymerization/HDO over Supported Ru Catalyst**
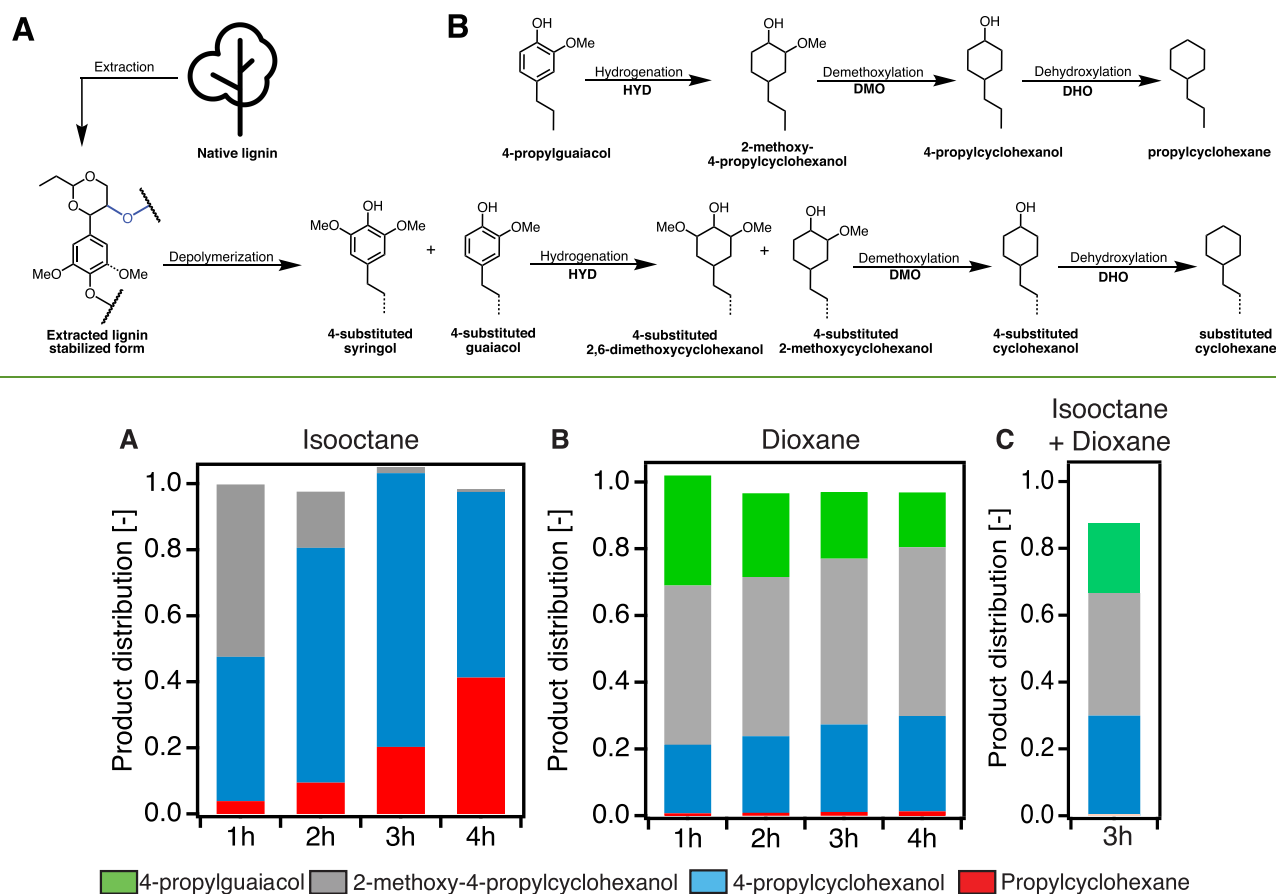




**Figure 1.** 4-Propylguaiacol HDO using Ru/C, 40 bar of $H_2$ at 250 °C (a) in isooctane, (b) in 1,4-dioxane, and (c) in isooctane in the presence of 1.3 $\mu$mol (0.22 mL) of 1,4-dioxane.

activity, it also greatly facilitates continuous processing. Meanwhile, despite the high solubility of isolated lignin in solvents such as 1,4-dioxane, there are no reports of HDO using this or other polar aprotic solvents that very effectively solubilize lignin. The oxygenated nature of such solvents may have limited the HDO activity, which, in turn, has limited the development of processes for deoxygenating lignin in such solvents.

A second reason limiting the study and development of catalytic processing of real lignin vs model compounds is that isolating pure unadulterated lignin is difficult. As has been frequently described, the conditions that are necessary to achieve lignin isolation from biomass lead to it rapidly condensing.[3,22,23] This condensation, which is thought to occur via dehydration and formation of a benzylic carbocation that reacts with nearby lignin aromatic groups, creates additional C−C linkages within lignin, lowering potential monomer production. For this reason, using isolated lignin typically leads to low monomer yields during catalytic processing (<10%).[3,24] Several groups have studied so-called "lignin-first" methods where the entire native biomass is reacted in the presence of the catalyst, which leads to direct hydrogenolysis of the lignin before it gets a chance to condense, leading to far better yields (40−50%, which is close to the theoretical yield based on ether cleavage).[4,25−27] However, the presence of the entire biomass prevents isolating any catalyst interaction with the lignin from that of the interactions with other biomass fractions, including (but not

limited to) the polysaccharides. The presence of these impurities could lead to similar aforementioned HDO activity suppression effects. Therefore, catalytic studies using real lignin have been limited by the use of either fundamentally altered lignin or native lignin in the presence of several other species.

Recently, we have shown that extracting lignin in the presence of aldehydes can prevent lignin condensation by forming acetals with the diols present in lignin's $\beta$−O−4 linkage, thus preventing dehydration reactions.[1] We have notably shown that this aldehyde-stabilized form of lignin can be isolated and purified while retaining its ability to be extracted at near theoretical yields (40−50%), indicating that the native linkages had been largely preserved.[28] Though this lignin contains acetals (see principal structure in Scheme 1A), its oligomeric structure is intact, and it is free from other biomass fractions, making it an ideal candidate for performing more detailed catalytic studies while avoiding issues of lignin degradation or external contaminants. As such, this substrate also offers a more natural comparison to model lignin monomers such as 4-propylguaiacol (PG).

## ■ RESULTS AND DISCUSSION

Here, we studied Ru-based catalysts and their ability to perform both lignin depolymerization and HDO of lignin using our isolated lignin (Scheme 1A) and compared it to PG HDO (Scheme 1B), which we used as a model for a lignin monomer. We specifically probe the effect of using oxygenated polar
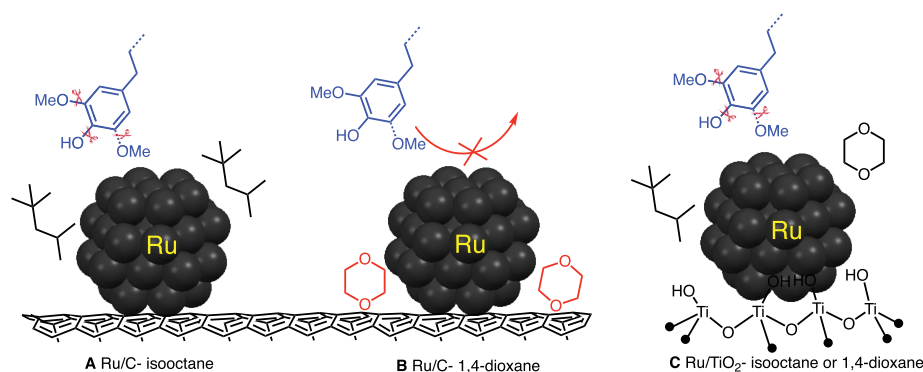
**Figure 2.** Illustration of the HDO process of 4-propylguaiacol and other lignin monomers on Ru NPs using carbon or TiO$_2$ as the support and isooctane or 1,4-dioxane as the solvent.

aprotic solvents such as 1,4-dioxane and the use of alternate supports to counter these solvent effects.

As a control, we performed a detailed study of solvent effects during PG HDO. With 40 bar of H$_2$ in isooctane at 250 °C in the presence of Ru/C, PG reacted rapidly, producing only ring hydrogenated molecules within the first hour and increasing quantities of full HDO products (propylcyclohexane) with increasing reaction time (Figure 1A). Ring hydrogenation is thermodynamically favored under such relatively high H$_2$ pressures and low temperatures. The hydrogenation product (2-methoxy-4-propylcyclohexanol) was initially detected and quickly converted to 4-propylcyclohexanol via demethoxylation, which is finally dehydrated and hydrogenated to the HDO product.

When switching from isooctane to using 1,4-dioxane, we observed incomplete conversion of the 4-propylguaiacol and much slower demethoxylation, while complete deoxygenation products were almost absent (Figure 1B). To further study the effect of 1,4-dioxane, we performed the reaction using isooctane as the solvent in the presence of a small amount (1.3 μmol in 10 mL) of 1,4-dioxane. The effect of using 1,4-dioxane as an additive was largely similar to its use as a solvent. Only 80% conversion was achieved after 3 h, and no propylcyclohexane was produced, suggesting that 1,4-dioxane acted as an inhibitor for HDO (Figure 1C). This phenomenon has been reported with polar aprotic solvents such as γ-butyrolactone or THF in hydrogenation of 2-butanone.[29] Wan et al. reported that during 2-butanone hydrogenation, Ru/C showed significantly higher activity in water, alcohol, and alkanes compared to in aprotic polar solvents. The authors proposed that aprotic polar solvents strongly adsorb onto the catalyst and block Ru's active sites.

Overall, studies with PG suggest that catalytic activity is strongly dependent on the presence of other oxygenated molecules, as Ru/C was able to perform full HDO in isooctane (Figure 2A), while little propylcyclohexane is detected when any 1,4-dioxane is present (Figure 2B).

To understand the substrate–support interaction's dependence on the solvent, we studied liquid phase PG adsorption on the support (activated carbon or AC) using isooctane and 1,4-dioxane as the solvents. We monitored the concentration of PG in solution by gas chromatography while dosing PG. Adsorption isotherms revealed that activated carbon adsorbed 9 times more PG in isooctane compared to in 1,4-dioxane, confirming the competitive adsorption of the oxygenated polar solvent on the support (Figure 3A). This trend followed the decreased HDO activity observed in the presence of 1,4-
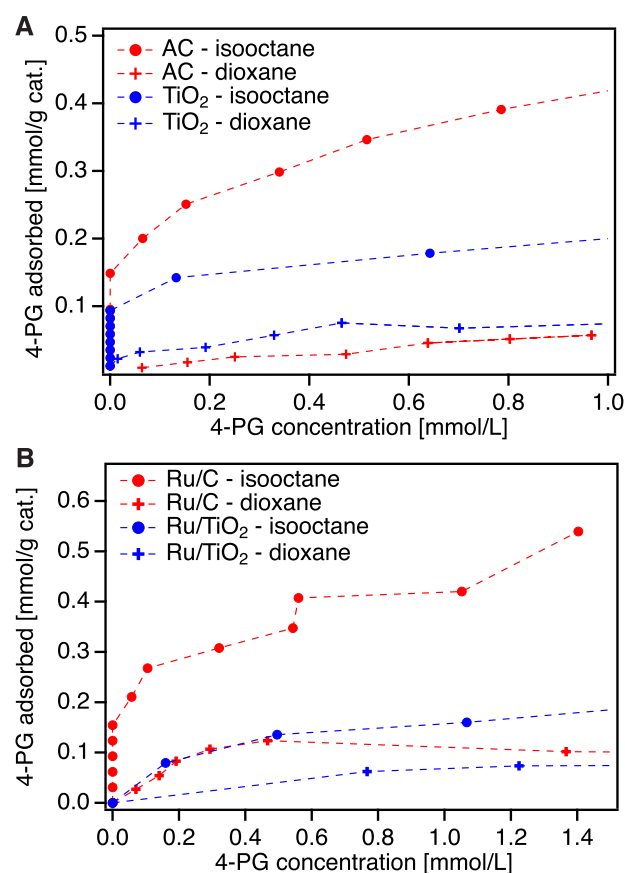


**Figure 3.** 4-Propylguaiacol adsorption isotherms in 1,4-dioxane and isooctane using TiO$_2$ and activated carbon (A) or Ru/C and Ru/TiO$_2$ (B).

dioxane. We also conducted the titration using the more oxophilic support TiO$_2$ (anatase). In isooctane, TiO$_2$ adsorbs approximately twice less PG than AC, mainly due to its lower surface area (catalyst properties are presented in Table S1). Interestingly, switching from isooctane to 1,4-dioxane when using TiO$_2$ as the support did not alter the adsorption capacity as drastically as it did for AC, with a 2-fold decrease only (Figure 3A). Ru NPs were likely passivated under adsorption conditions, and similar trends were observed after deposition of Ru on these respective supports (Figure 3B). Hence, the competitive adsorption effect of 1,4-dioxane on the catalyst was less pronounced when using TiO$_2$. We could not tease out whether this beneficial support effect on PG adsorption
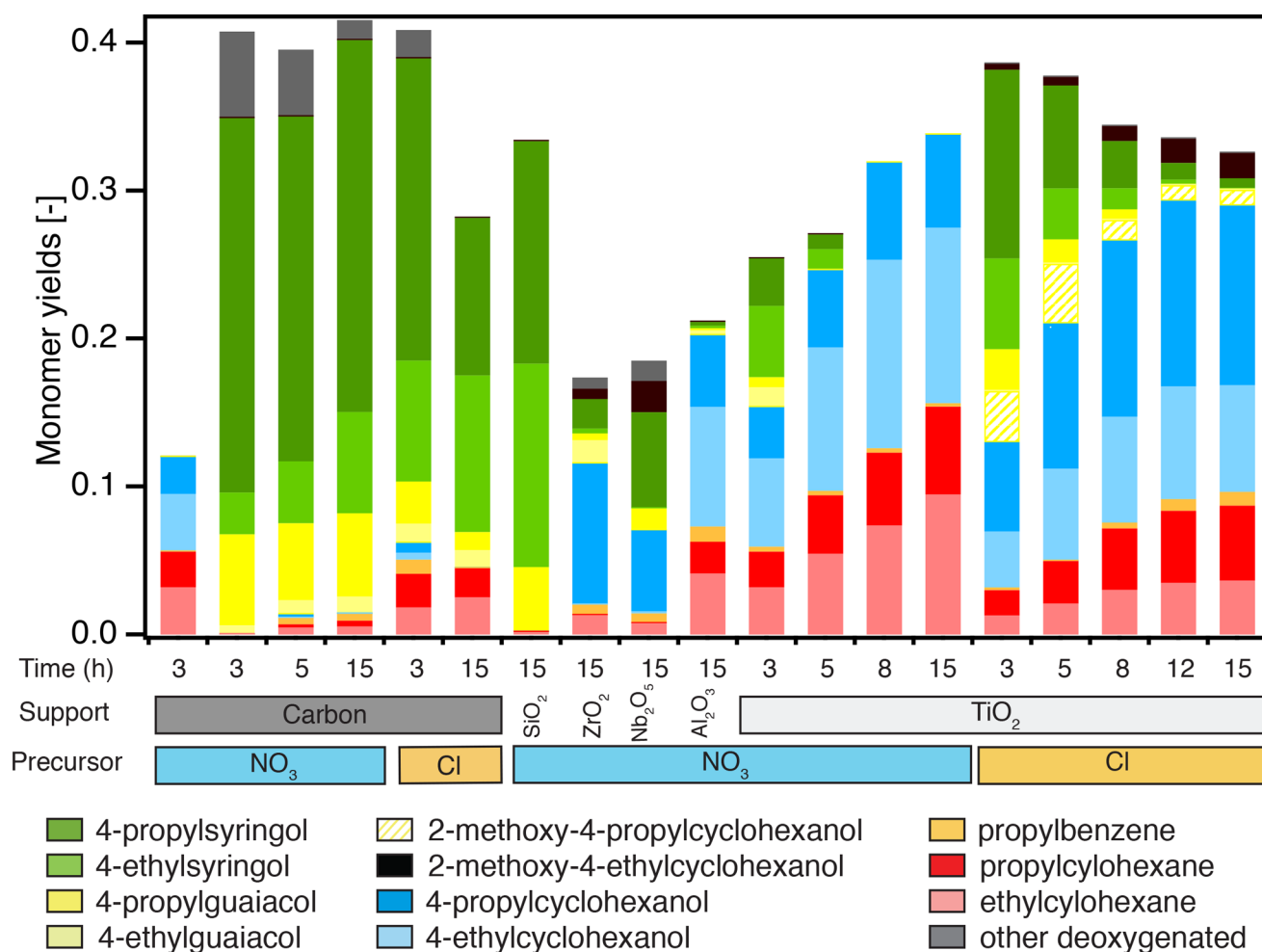
**Figure 4.** Product distributions during the combined depolymerization and HDO of isolated propionaldehyde-stabilized lignin over Ru catalysts. Reaction conditions: 250 °C, 40 bar of H$_2$, 50 mg of catalyst, 100 mg of lignin, and 400 rpm; the reaction time is indicated below each bar. The solvent was 1,4-dioxane, except for the first bar where isooctane was used.

behavior was occurring just on the support or on the support and the metal, since there is most likely competitive adsorption of solvent on Ru and the support. However, we suspect that even if we are only able to increase PG adsorption on the support, this could increase the HDO activity through HDO catalysis at the metal support interface, which has been suggested to occur.[30] Overall, these results suggest that combining lignin depolymerization with HDO in a lignin friendly solvent like 1,4-dioxane might be possible using TiO$_2$ as a support.

To test this hypothesis, we explored the use of Ru to catalyze both the depolymerization and HDO of isolated aldehyde-stabilized lignin extracted from beech wood in the presence of propionaldehyde. In this process, stabilized lignin was likely first depolymerized into its corresponding monomers, which were methoxylated and alkylated phenols (lignin's stabilized β−O−4 linkage, which is the main moiety in our isolated lignin, along with its subsequent depolymerization and HDO pathway are shown in Scheme 1A). Further hydrogenation led to ring saturation followed by the production of substituted cyclohexanols. Demethoxylated phenolic products or alkylated benzene derivatives were generally minority products due to the propensity of Ru to hydrogenate the ring. Similarly, few methoxylated products were observed once some HDO activity was present, because removing methoxy groups is

less energy-intensive than removing the phenolic hydroxyl group (we refer to demethoxylation products as DMO products).[17,31] These intermediates can undergo further oxygen removal to form substituted cyclohexanes (through dehydroxylation (DHO) products).

The specific reaction conditions we used involved reacting lignin with 40 bar of H$_2$ at 250 °C in the presence of Ru-based catalysts deposited on activated carbon or various metal oxides. The catalysts were prepared by impregnation using either RuCl$_3$ or Ru(NO$_3$)$_3$ as a precursor followed by nanoparticle formation under hydrogen at 300 °C. All catalysts had a 5 wt % Ru loading and a mean NP size between 1 and 2.4 nm (NP size distributions and transmission electron micrographs are shown in Figure S1). Minor changes in the Ru NP dispersion can result in significant selectivity changes, since structure insensitive reactions (e.g., hydrogenation of benzene) compete with structure sensitive reactions (e.g., hydrogenolysis of C−C and C−O bonds occurring on an assembly of surface metal atoms). This was notably reported for phenol HDO using Ni/SiO$_2$[32] or hydrogenolysis of lignin model compounds using Ru/NbOPO$_4$.[33] However, in our case, the observed HDO selectivities did not correlate with Ru NP size (Figure S5), confirming the importance of the support and solvent on HDO reactions.

We began by testing depolymerization and HDO in isooctane, as it was the best HDO solvent for PG. However, the process was limited by lignin's solubility in a three phase, solid−solid−liquid system, leading to a yield of only 13% monomers after 3 h (Figure 4). The product mixture consisted of an equimolar distribution of cyclohexanes and cyclohexanol. The absence of any guaiacols and syringols suggested that HYD and DMO rates far exceeded depolymerization rates. Monomer yield is calculated as the molar ratio of aromatics produced over the quantity of aromatic units in lignin before reaction (see section S1.5 of the Supporting Information). As several groups have shown, by performing a direct hydrogenolysis on untreated biomass, close to all of native lignin's ether bonds are cleaved, resulting in a monomer yield that is close to theoretical.[12,27,28] In this case, we achieved a monomer yield of 46%, which is around the maximum that would be expected based on total ether cleavage and can be assumed as the maximal achievable yield in the discussion below.

In order to avoid the aforementioned lignin dissolution issues and to enable combined lignin depolymerization/HDO under continuous operation, we used 1,4-dioxane to solubilize our stabilized lignin. Using 1,4-dioxane as the solvent led to a monomer yield of 42% after 3 h, which was close to the aforementioned maximum achievable yield. The products were a mixture of alkylsubstituted guaiacols and syringols in agreement with our previous report[5,28] (Figure 4). When prolonging the reaction time to 15 h, only 2% HDO products were observed. Hence, only depolymerization and little hydrodeoxygenation occurred under these conditions.

Interestingly, an HDO yield of 5% was reached within 3 h when using Ru/C synthesized from $RuCl_3$, but a longer reaction time did not improve HDO and even reduced overall yields. This increase in HDO activity could be due the generation of oxophilic surface sites on carbon when using a chlorinated salt during catalyst preparation. Promotion of transition metal catalytic activity by chlorine has been suggested for CO hydrogenation.[34] Among the metal oxide supports that were tested, $SiO_2$ did not show significant HDO activity, in line with its low acidity and oxophilicity. Switching to $ZrO_2$ or $Nb_2O_5$ resulted in significant demethoxylation but little HDO activity, while selectivities of 55% DMO and 30% HDO products were achieved using $Al_2O_3$ as the support. However, the support leading to by far the highest quantity of HDO products was $TiO_2$ with a proportion of fully deoxygenated products reaching 50% after 15 h, the remaining being DMO products. This result is in line with the improved ability of Ru/$TiO_2$ to perform HDO on PG compared to Ru/C (Figure S3). $TiO_2$'s outstanding activity was attributed to both its C−O bond activation thanks to the reactant's Ti−O interaction but also its aforementioned ability to improve monomer adsorption even in the presence of an oxygenated solvent. When preparing Ru/$TiO_2$ from the $RuCl_3$ precursor, 37% of the overall yield could be achieved within 3 h, but the selectivity to HDO products reached a maximum after 15 h at 30%, compared to 50% when preparing Ru/$TiO_2$ from Ru$(NO_3)_3$. Hence, while the use of a chlorine Ru precursor on carbon promoted HDO activity by creating oxophilic sites, electron-rich chlorine could have acted as an inhibitor when using $TiO_2$ as the support by passivating Lewis acid sites, which are known to assist HDO.[9,35] Support pore size distribution was calculated using the BJH model with $N_2$ desorption isotherms (Figure S2). Diffusion of the bulky lignin polymer, which could reach several nanometers in length, is

potentially slower in microporous (e.g., carbon with an average pore size of 4 nm) compared to mesoporous supports (e.g., $TiO_2$ with an average pore size of 9 nm). Nevertheless, lignin depolymerization was systematically faster than HDO, as we always observed high monomer yields even at short reaction times with carbon supports. In contrast, the oxygenated monomers undergoing HDO are systematically smaller than 1 nm and are thus unlikely to be affected by pore size effects. Furthermore, the absence of mass transfer limitation between the bulk solution and the surface of the catalyst was confirmed by estimating the Weisz−Prater criterion (section S2).

Finally, we tested the ability of Ru/$TiO_2$ to perform lignin HDO in the presence of $C_5$ sugars and other biomass derivatives. A reaction was performed on extracted liquor after neutralization and without lignin isolation, the largest component of which is $C_5$ sugars. No HDO products were detected, suggesting the further inhibitory effect of $C_5$ sugars and other biomass-derived impurities from the liquor (Figure S4). This underlies the importance of lignin isolation to eliminate catalyst poisoning effects attributed to side products encountered when using raw extracted liquor. In addition, the hydrogenation of propanal-protected lignin produces propanol, but this byproduct equally impacts all catalytic tests and seems to have a limited effect on HDO activity.

## ■ CONCLUSION

In summary, of the many studies attempting to deoxygenate lignin, most focus on phenolic model compounds and are quite successful in removing oxygen when working in the gas phase or using alkanes as solvents. Liquid phase titrations of 4-propylguaiacol in various solvents demonstrated that high HDO yields are strongly correlated with the ability of these phenolic monomers to adsorb on the catalyst and its support, which is strongly curtailed in the presence of the oxygenated solvents that can actually dissolve real lignin or other biomass-derived components including $C_5$ sugars or impurities. Switching to an oxophilic support such as $TiO_2$ significantly reduced the competitive binding of the solvent on the support and allowed increased access of the catalyst to the phenolic monomers. This access significantly increased the demethoxylation and eventual HDO of phenolic monomers even when real lignin was used as the reactant. These results explain known differences between hydrogenation of real lignin and model compounds and offer catalyst design strategies for producing deoxygenated molecules from lignin in a single step.

## ■ ASSOCIATED CONTENT

### ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b03843.

> Chemicals and materials, experimental procedure for catalyst preparation, catalyst characterization, catalytic testing (PDF)

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