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On the reactivity of dehydro-*p*-coumaryl alcohol towards reductive processes catalyzed by Raney Ni

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Abstract: There are several established approaches for the reductive fractionation of lignocellulose (e.g. 'catalytic upstream biorefining' -CUB, or 'lignin-first' approaches) that render a lignin oil product composed primarily of dehydro-p-monolignols (e.g. 4-(3-hydroxypropyl)-2-methoxyphenol, 4-(3-hydroxypropyl)-2,6-dimethoxyphenol). Although effective catalytic methods have been developed in order to perform reductive or deoxygenative processes on the lignin oil, the influence of the 3-hydroxypropyl substituent on catalyst activity has previously been overlooked. Herein, to better understand the reactivity of the depolymerized lignin oil obtained from catalytic upstream biorefining processes, dehydro-p-coumaryl alcohol is selected as a model compound. Hydrogenation of this species in the presence of Raney Ni with molecular hydrogen leads to ring saturation (100% selectivity) in the absence of hydrodeoxygenation, whereas under hydrogen transfer conditions with 2-propanol, hydrogenation occurs (ca. 55% selectivity) simultaneously with hydrodeoxygenation (ca. 40% selectivity). In a broader context, this study sheds light not only on the reactivity of dehydro-p-monolignols but also on the intricacies of the CUB reaction network in which these species are revealed to be key intermediates in the formation of less functionalized p-alkylphenols.

Undoubtedly, lignin constitutes the primary renewable source of bulk and specialty aromatic chemicals.^[1] Recently, several catalytic routes have been developed to convert lignocellulosic biomass into a mixture of compounds that show potential to replace petroleum-based raw materials.^[2] In this context, the emerging field of 'catalytic upstream biorefining' (CUB, sometimes referred to as 'reductive fractionation' or the 'lignin-first' approach) has attracted increasing attention.^[1a, 3] CUB encompasses processes for plant biomass deconstruction through the early-stage catalytic conversion of lignin (ECCL) by the action of a hydrogenation catalyst.^[1a] In our CUB process, based on the ECCL of lignin by hydrogen-transfer (H-transfer) reactions catalyzed by Raney Ni, the lignin fraction is isolated as a viscous oil.^[4] This lignin stream is rich in monophenolic species (< 65%). Notably, the type of functional groups on the propyl sidechain of the monophenolic compounds depends both on the selected catalyst and the hydrogen source employed in the process.^[4a, 5] Furthermore, the lignin oil also contains dimers and low-molecular-weight lignin oligomers $(M_w < 1,000 \text{ Da})$, as minor products (> 35%). Amid the

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Department of Chemical Engineering, Imperial College London, South Kensington Campus, SW7 2AZ London (UK) E-mail: rrinaldi@ic.ac.uk monophenolic products obtained by H-transfer CUB in the presence of Raney Ni, two major products — dihydro-*p*-sinapyl alcohol (1, Fig. 1) and dihydro-*p*-coniferyl alcohol (2, Fig. 1) — are obtained from the biorefining of hardwoods. Understandably, the CUB of softwoods generates 2 as the major product.

Products 1 and 2 incorporate three classes of oxygenated functional group, namely: (i) the phenolic -OH substituent; (ii) the methoxy group(s) ortho to the phenolic -OH group, and; (iii) the primary alcohol at the y-position of the propyl sidechain. While catalytic transformations of model compounds entailing the first two functional groups (e.g. guaiacol derivatives) have been the motivation for numerous insightful studies in catalysis for lignin valorization,^[1b, 6] little is known about the conversion of 1 or 2 in the presence of a heterogeneous catalyst. Our previous studies revealed that the hydrogenation activity of Raney Ni is dramatically inhibited by using primary alcohols as reaction solvents.^[7] Among the main reasons accounting for this observation, the high affinity of primary alcohols towards the catalyst surface seems to be the factor responsible for the decreased performance of Raney Ni in these solvents.^[7-8] Therefore, it is to be expected that conversion of dehydro-p-monolignols would be hindered by the presence of the γ -CH₂OH group.



Figure 1 The two most abundant phenolic products present in lignin oils obtained from H-transfer CUB processes performed in the presence of Raney Ni and 2-propanol (H-donor and component of the liquor) – dehydro-*p*-sinapyl alcohol (1) and dehydro-*p*-coniferyl alcohol (2) – alongside model compound dehydro-*p*-coumaryl alcohol (3).

In this communication, we explore the effect of the γ -CH₂OH substituent on the reactivity of dehydro-*p*-coumaryl alcohol (**3**, corresponding to lignin H-units) in reductive processes catalyzed by Raney Ni, under H₂ pressure, as well as under H-transfer conditions solely using 2-propanol (2-PrOH) as the H-donor. The reason underlining the choice of **3** (instead of **1** or **2**) is the absence of labile methoxy groups as a substituent on the phenolic ring. In the presence of Raney Ni using 2-PrOH as the solvent and H-donor, *o*-methoxyphenols easily undergo demethoxylation via H-transfer processes, releasing MeOH. In the reaction medium, the presence of MeOH perturbs the H-transfer reactions and may bias the results regarding the precise effect of the γ -CH₂OH group upon substrate reactivity. Using compound **3** as a model, the specific influence of the γ -CH₂OH substituent may, therefore, be pinpointed specifically without the interference of MeOH.

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Table 1 summarizes the product distributions for hydrogenation of **3**, with H_2 gas, and through H-transfer reactions using 2-PrOH as the sole H-source.

Table 1. Catalytic reduction of dehydro-p-coumaryl alcohol, 3, using H₂ gas, and via H-transfer reactions using 2-PrOH as an H-donor.



Reaction conditions: [a] substrate (3 mmol), solvent (2-PrOH, 15 mL), stirring rate: 300 rpm; [b] substrate (2 mmol), solvent and H-donor (2-PrOH, 8 mL), stirring rate: 800 rpm.

In the presence of H₂, the substrate underwent hydrogenation selectively to render the diol 4-(3-hvdroxvpropyl)cvclohexan-1-ol (4) as the product (entry 1). In the absence of H_2 , the conversion fell from 25% to just 5% (entry 2). Surprisingly when 2-PrOH was used as the sole H-source, the diol 4 was no longer the exclusive product, but 4-propylphenol (5) and 4-ethylphenol (6) were also present in the product mixture in high concentrations (entry 2). To achieve a higher conversion in the H-transfer reaction, the loading of Raney Ni was increased (from 0.1 to 1 g, entry 3). Under this condition, a 78% conversion at 80 °C was achieved after 3 h. However, the reaction selectivity remained unchanged regardless of the catalyst amount present in the reaction (entries 2 and 3). This result clearly indicates that products 4, 5 and 6 are formed by parallel reactions. The parallel reactions are proposed to be a consequence of the formation of distinct adsorption complexes of 3 on the surface of Raney Ni. From the current experimental evidence, one population of the adsorbed molecules appears to interact with the surface via the formation of a phenolate surface species (Fig. 2a), involving the interactions of both phenolic -OH substituent and aromatic ring with the surface. In agreement with a previous report,^[9] the planar adsorption of phenol on the Ni surface favors hydrogenation. Therefore, this surface species (Fig. 2a) undergoes hydrogenation, yielding 4 as the product. Hypothetically, the other population of adsorbed molecules interacts with the surface through the formation of an alkoxide species involving the y-CH₂OH group in addition to the phenolate interaction (Fig. 2b). Indeed, adsorption on the nickel surface brings about dehydrogenation of methanol to coadsorbed methoxy (CH₃O) and hydrogen species.[10]

To better understand the reactivity of the γ -CH₂OH substituent in conjunction with aromatic moieties, another model compound, 3-phenylpropanol, was investigated with respect to transfer hydrogenation. The overall conversion and product distribution is shown in Scheme 1, compared against the results of the reaction involving phenolic analog **3**.



Figure 2 Schematic representation of proposed interaction motifs of dehydrop-coumaryl alcohol with an idealized Ni surface: (A) an adsorption complex involving interactions of the phenolic –OH group and ring with the surface; (B) an adsorption complex established via the interactions of the γ -CH₂OH alcohol group in addition to the phenolic –OH group and ring with the surface.









Under the same reaction conditions, the conversion of 3-phenylpropanol (70%) was slightly lower than that of 3 (78%). Surprisingly, the conversion of 3-phenylpropanol afforded a yield of arene products twice as high as that obtained from the conversion of 3. In particular, n-propylbenzene accounted for 72% of the product mixture obtained from 3-phenylpropanol. For both reactions, the accumulation of arenes in the reaction mixture agrees well with previous results demonstrating that aromatic hydrocarbons are far less reactive than phenols with respect to ring saturation via transfer hydrogenation.^[8] Hence, if the tendency towards hydrogenation of the aromatic ring is decreased from 3 to 3-phenylpropanol, the rate of the deoxygenation of the propyl chain is increased. As a result, deoxygenation occurs with the formation of a high yield of *n*-propylbenzene and a lower quantity of ethylbenzene. As evidenced by several studies, the interaction between Ni surfaces and primary -OH alcohol groups is stronger than that of Raney Ni and secondary alcohols.^[7-8] In this manner, the γ-CH₂OH group could also serve as a source of hydrogen for H-transfer processes.

Taking this hypothesis into account, we chose to perform an additional catalytic experiment on hydrocinnamaldehyde. This model compound corresponds to an intermediate that may be postulated to exist on the Raney Ni surface *via* the donation of

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two H atoms from 3-phenylpropanol to the surface. The overall conversion and product distribution are shown in Scheme 2. Hydrocinnamaldehyde was converted in 90% yield, affording the primary products 3-phenylpropanol (43%) and ethylbenzene (20%). Notably, the mass balance was not fully closed. Only ca. 65% of the starting carbon could be accounted for in the products. Condensation reactions could explain this observation, because such high M_w -products would not be identifiable by GC-MS/FID.

Hydrogenation and elimination reactions of the aldehyde group were found to proceed as parallel processes (Scheme 2). However, hydrogenation of the carbonyl group was favored over the deoxygenation process via elimination of the aldehydic group. Notably, selectivity toward *n*-propylbenzene was relatively low (ca. 2%). This result clearly demonstrates that the formation of ethylbenzene from 3-phenylpropanol (Scheme 1) occurs *via* dehydrogenation of the primary alcohol, forming an aldehyde intermediate, which decomposes into ethylbenzene. It can generally be stated that hydrogen has an influence on the reaction pathway.^[10] It is here shown that in the absence of the hydrogen pressure, hydrogenation of the aromatic ring becoming less favorable, and deoxygenation becomes increasingly significant.

Although this pathway is plausible, further reaction of the aldehyde to the corresponding carboxylic acid, and subsequently decarboxylation of the carboxylic acid may also lead to the ethylsubstituted cyclic compounds.^[11] However, in a previous study, we found that benzoic acid is readily and quantitatively converted into cyclohexanecarboxylic acid in the presence of Raney Ni/2-PrOH at 80 °C, within 3 h.^[8] In comparison, benzaldehyde exhibits a similar pattern of reactivity to that of hydrocinnamaldehyde, that is, hydrogenation of the aldehyde substituent, rendering benzyl alcohol, taking place in parallel with the hydrodeoxygenation of benzaldehyde to toluene.^[8] Therefore, as no carboxylic acid was detected in the product mixture arising from the conversion of hydrocinnamaldehyde, its further dehydrogenation generating hydrocinnamic acid seems not to occur under the reaction conditions. Cracking of the alkyl chain could also, in principle, lead to the formation of the p-ethyl derivative. However, such a cracking reaction is only reported to occur at higher temperatures (over 200 °C).^[12] Moreover, the reactions of various alkylated phenols on Raney Ni, with 2-PrOH as a hydrogen source at 80 °C (same condition of reaction as for the hydrogenation of 3),^[8] do not lead to any detected products derived from cracking of the alkyl chain.

In an attempt to establish a rank of interaction strengths of 2-PrOH (H-donor), methanol (a model of the γ -CH₂OH group in **3**), and phenol with the Raney Ni surface, competitive adsorptions of 2-PrOH vs. MeOH and phenol vs. MeOH at the catalytic solidliquid interface were evaluated (25 °C), by using an Attenuated Total Reflection-Infrared (ATR-IR) spectroscopy setup. In these experiments, a film of Raney Ni was deposited on a ZnSe crystal under an argon atmosphere. A background spectrum was collected under a flow of cyclohexane. In sequence, the catalyst was flushed with a 5 mM solution of 2-PrOH in cyclohexane or a 1 mM solution of phenol in cyclohexane. To remove dissolvedphase species, the cell was flushed again with cyclohexane, and the spectrum was collected. Finally, in each experiment, the initial solution was then exchanged with an analogous solution containing an additional 2 mM MeOH (in the case of 2-PrOH) or 1 mM MeOH (in the case of phenol), and the spectra were collected after flushing the catalyst bed with cyclohexane.

Figure 3 displays the ATR-IR spectra of strongly adsorbed species at the catalytic solid-liquid interface at 25 °C. A decrease in signal intensity of the characteristic vibration bands of 2-PrOH was caused by the presence of MeOH in the solution. Conversely, Figure 3b shows that the signal intensities of the characteristic vibration bands of phenol were not affected by the presence of MeOH. These observations demonstrate that MeOH can displace 2-PrOH from the Raney Ni surface, whereas MeOH and phenol can co-adsorb without affecting the populations of one another on the surface.

In light of the current results, the adsorption complex 'B,' as proposed in Figure 2, seems to be a plausible proposition of the interactions of **3** occurring at the catalytic solid-liquid interface under the absence of an H₂ pressure. Notably, the current results demonstrate that interaction of the γ -CH₂OH substituent does not depend upon interactions of the phenolic/aromatic ring with the surface. The catalytic results showing that the γ -CH₂OH group undergoes dehydrogenation, forming an intermediate aldehyde, corroborate with the preferential interactions established between a primary alcohol group and the Raney Ni surface, which largely compete with those interactions established between 2-PrOH and the catalytic surface.



Figure 3 Competitive adsorption of a) 2-PrOH vs. MeOH, and; b) phenol and MeOH on the surface of Raney Ni at 25 °C. Blue arrows indicate a decrease in the signal intensity of the characteristic bands of adsorbed 2-PrOH at the catalytic solid-liquid interface.

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From the observations of this study, the three parallel reaction processes occurring for dehydro-p-coumaryl alcohol, using 2-PrOH as the H-donor and solvent in the presence of Raney Ni, can be summarized in Scheme 3. In process (A), saturation of the phenolic ring is achieved. This pathway predominates under Htransfer conditions but is not exclusively followed (56% selectivity to diol). By contrast, under H₂ pressure, this reaction brings about 100% selectively to the diol product. Under both conditions, the diol 4 cannot undergo a further transformation in the presence of Raney Ni. Processes (B) and (C) are parallel reactions occurring only under H-transfer conditions. Through pathway (B), the C-O bond of the γ-CH₂OH group is hydrogenolyzed, leading to the formation of 4-propylphenol at a selectivity of 32%. In turn, the reaction process (C) is a competing reaction, forming an aldehyde intermediate via dehydrogenation of dehydro-p-coumaryl alcohol, and subsequent elimination of the aldehyde group, most likely as formaldehyde.

Clearly, the suppression of reaction processes (B) and (C) when the reaction is carried out under H₂ pressure reveals that even under low-severity conditions (e.g. 5 MPa H₂ at 90 °C), the surface chemistry of Raney Ni can be substantially altered. As revealed by Ni X-ray Photoelectron Spectroscopy (XPS) experiments (Figure 4), the surface of freshly synthesized Raney Ni shows at least three major Ni surface species: Ni(0) at 852.6 eV, Ni(II)-OH at 855.8 eV, and an unassigned species at a higher binding energy (857 eV, most likely related to NiOx(OH)v species).^[13] Our results suggest that the proportion of these species may vary substantially under H₂ pressure at temperatures as low as 90 °C. Moreover, the accumulation of 4-alkylphenols in the product mixture is a key feature starkly contrasting to our previous studies, which demonstrated that 4-propylphenol fully converts into 4-propylcyclohexanol under low-severity conditions.^[8] The current results also suggest that, when reacted in a system composed of 2-PrOH/Raney Ni, the substrate 3 not only inhibits the activity of Raney Ni towards the saturation of the phenolic ring but also seems to modify the surface structure of Raney Ni, making it no longer active for the catalytic processes leading to the hydrogenation of the phenolic ring by H-transfer processes at temperatures as low as 80 °C.

In the broader context of heterogeneous catalysis, the confirmation of these hypotheses would reveal a somehow surprising feature of Raney Ni. As well-known from the experience of supported Ni catalyst preparation, Ni(II) reduction to Ni(0) species usually takes places at temperatures higher than 200 °C, for Ni(II) supported on activated carbon or inorganic carriers.^[14] Accordingly, the ease of reduction of the Raney Ni surface, as revealed by the change of selectivity to the exclusive saturation of the phenolic ring, seems to be a feature of Raney Ni distinguishing it from supported Ni catalysts.

In summary, dehydro-*p*-coumaryl alcohol exhibits distinctly different reactivity patterns toward reductive processes catalyzed by Raney Ni, when performed under H-transfer conditions or H₂ pressure. Evident lines of investigation for the future are high-pressure XPS, XANES and XRD studies under *operando* conditions to lend insight into the functionality of the surface structure of the *real* Raney Ni catalyst. Nonetheless, the current results clarify the origin of C₇-C₉-alkylphenols formed as minor products in the CUB process based on H-transfer ECCL in the presence of Raney Ni. In a broader context, the current results also point out

new directions for the valorization of the lignin oil obtained from CUB processes. As several CUB processes produce dehydro-*p*-monolignols as major products, the selective hydrogenation of these intermediates to the corresponding diols could well hold the key to obtaining lignin-derived long-chain diol monomers as replacements for petroleum-derived 1,6-hexanediol, employed on the large-scale production of polyesters.



Scheme 3 Reaction processes resulting in the conversion of dehydro-*p*coumaryl alcohol in the presence of Raney Ni and 2-PrOH (as the solvent and H-donor).



Figure 4 X-ray Photoelectron Spectroscopy spectrum of a freshly prepared sample of Raney Ni.

Experimental Section

Chemicals

2-Propanol (99.8%), dehydro-*p*-coumaryl alcohol (99%), *n*-hexadecane (99%), Raney Ni 2800, 3-phenylpropanol (Aldrich, 98%), and hydrocinnamaldehyde (>95%) were purchased from Aldrich and used as received.

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Hydrogenation of dehydro-p-coumaryl alcohol with H₂

Dehydro-*p*-coumaryl alcohol (2.9 mmol), hexadecane (internal standard for GC, 0.78 mmol), Raney Ni 2800 (dry 100 mg, pre-dried under reductive pressure using Schlenk techniques), and 2-PrOH as the solvent (15 mL) were placed in a batch reactor (30 mL) under an argon atmosphere (glove box). After purging the reactor with H₂, the reaction vessel was loaded with 5 MPa H₂ (measured at 25 °C). The reaction temperature was increased from r.t. to 90 °C at a rate of 7 °C min⁻¹, and was then maintained at 90 °C for 2.5 h, applying overhead mechanical stirring throughout (300 rpm).

Hydrogen transfer reaction of dehydro-*p*-coumaryl alcohol, 3-phenylpropanol, and hydrocinnamaldehyde with 2-PrOH

Dehydro-*p*-coumaryl alcohol, 3-phenylpropanol or hydrocinnamaldehyde (2.1 mmol), *n*-hexadecane (internal standard for GC, 0.8 mmol), Raney Ni 2800 (1 g, wet), solvent (7 mL) and a magnetic stirrer bar were placed in a glass vial (20 mL). The vial was flushed with argon and then tightly closed. The experiment was performed at 80 °C under magnetic stirring (800 rpm) in a stainless steel heating block for 3 h.

GC-MS/FID analysis

The samples were analyzed by GC using a Shimadzu QP2010 Plus gas chromatograph, equipped with a ZB-1HT Inferno column (30 m, 0.25 mm ID, df 0.25 µm). The injector temperature was 300 °C. The temperature program started at 40 °C for one minute. Next, the temperature was increased at 8 °C min⁻¹ to 140 °C, then increased at 20 °C min⁻¹ to 180 °C and then again raised at 30 °C min⁻¹ before reaching an isothermal step at 340 °C for 5 min. The compounds were identified by comparing the EI-MS spectra with the MS libraries NIST 08, NIST 08s, and Wiley 9. Quantification was performed using the response of the FID.

In situ ATR-IR spectroscopic measurements

The in situ ATR-IR spectroscopic measurements were performed using a custom-built set-up.^[15] A thin film of Raney Ni was deposited onto a ZnSe crystal in a custom built mini glove-box by shaking a hexane solution containing Raney Ni and pouring the suspension into a form as described in Ref. [15]. The film was then sealed into the ATR-IR spectroscopic flowthrough cell under an argon atmosphere and was transferred to the continuous flow set-up.^[15] The argon was removed from the cell with a cyclohexane solution at a flow rate of 0.5 mL min-1, after which the flow rate was increased to 2.7 mL min-1. A background spectrum was collected under a convective flow of cyclohexane at a flow rate of 2.7 mL min⁻¹. For the adsorption experiments, the film was treated with a 1 mM phenol solution (5 mM in the case of 2-PrOH) in cyclohexane. The cell was again flushed with cyclohexane, removing the dissolved-phase of phenol and leaving only the strongly adsorbed species, which could not be removed by a convective flow of cyclohexane. In each experiment, the initial solution was then exchanged with an analogous solution containing an additional 2 mM MeOH (in the case of 2-PrOH) or 1 mM MeOH (in the case of phenol), and the spectra were collected after flushing the catalyst bed with cyclohexane.

XPS analysis of Raney Ni

In a glove-box under argon atmosphere, the dry Raney Ni powder was distributed uniformly on a carbon tape fixed on an XPS sample holder for air-sensitive samples. The holder was closed and transferred to the XPS pre-chamber. XPS analysis was performed using a 'Kratos His' spectrometer with a hemispherical analyzer. The monochromatized Al_{Ka} X-ray source (E =1486.6 eV) was operated at 15 kV and 15 mA. For the narrow scans, an analyzer pass energy of 40 eV was applied. The hybrid mode was used as the lens mode. The base pressure during the experiment in the analysis chamber was 4.10⁻⁷ Pa. To account for charging effects, the spectra were referred against C_{1s} at 284.5 eV.

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Keywords: lignin • Raney Ni • catalytic upstream biorefining • hydrodeoxygenation • hydrogen transfer

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Fifty shades of green. The advent of catalytic upstream biorefining has made available new platform chemicals from lignin. In this communication, the reactivity of dehydro-p-coumaryl alcohol is explored in reductive processes catalyzed by Raney Ni, under H₂ pressure as well as under H-transfer conditions. Under H₂ pressure, Raney Ni is a selective hydrogenation catalyst. However, under H-transfer conditions, the catalyst also produces 4-alkylphenols.



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