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ARTICLE

One-pot Hydrodeoxygenation (HDO) of Lignin Monomers to C9 Hydrocarbons co-catalysed by Ru/C and Nb_2O_5

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A physical mixture of Ru/C and Nb_2O_5 is an effective catalyst for upgrading lignin monomers under low H_2 pressure at 250 ℃ to a clean cut of hydrocarbon liquid fuel. The reaction solvent is water with a small amount of methanol additive. The hydrodeoxygenation (HDO) was evaluated by using dihydroeugenol (DHE) as an exemplary model lignin monomer. Under optimized conditions, 100% conversion of DHE and very high selectivity to propyl cyclohexane (C9 hydrocarbon) was achieved. The Nb_2O_5 was prepared at low temperature (450 ℃) and was shown to contain acid sites that enhance the production of fully deoxygenated product. The methanol additive serves as hydrogen source for the Ru/C catalysed reduction of the aromatic ring. In addition, when a substrate mixture of DHE, isoeugenol and 4-allylsyringol simulating lignin products was employed, 100% conversion to propyl cyclohexane (76%) and propyl benzene (24%) was observed, thereby suggesting the general applicability of this catalyst system for funneling lignin monomers into a clean slate of hydrocarbon liquid fuels.This study sheds light on the function of each catalyst component and provides a simple and green utilization of biomass monomers as a feedstock for renewable hydrocarbon fuels.

Introduction

Non-renewable fossil carbon has been the main resource to produce most chemicals and fuels for the past century; however, renewable alternatives are available. Lignocellulose is by far the most abundant renewable source of non-food-based carbon, and there is considerable interest in upgrading such biomass as a sustainable feedstock.[1-5] The lignin component of lignocellulose is the second most plentiful biopolymer in nature (after cellulose), has a high carbon content, and is (potentially) the largest renewable resource of aromatic chemicals and fuels.[5-9] However, it has an irregular structure with random linkages between monomeric components having different levels of oxygenation that is challenging to utilize chemically.[10] Due to this dilemma, pulp, and paper industries and biorefineries typically dispose of lignin by burning it. Thus, lignin is an attractive target for biomass valorisation.

Lignin can be converted to bio-oil as a renewable liquid fuel.[11] However, bio-oils cannot be used in conventional gasoline and diesel fuel engines due to the high oxygen content [up to 60 weight % (wt %)] that makes them immiscible with petroleum-derived fuels.[12, 13] Thus, oxygen removal while maintaining the carbon structures has the potential to enhance the utilization of bio-oil as a transportation fuel.

Catalytic hydrodeoxygenation (HDO) can upgrade bio-oils. In most studies, HDO involves treatment at high temperatures (250-500 ℃) with high pressure of H_2 (50-100 bar). The high pressures required may limit the scalability of the reaction and is a safety hazard.[14] These obstacles encourage the research towards alternative approaches for phenolic upgrading under milder conditions.

The goal of the present study is to develop catalytic strategies that efficiently funnel lignin disassembly components into a narrowly defined product stream useful as a feedstock for the synthesis of aromatic chemicals (C6-C9 aromatic hydrocarbons) or as drop-in biofuels. Phenolics would be desirable for the former processes, while oxygen-free hydrocarbons that can replace fossil-carbon liquid fuels would serve the latter purpose.[15-17] In previous studies, various types of heterogeneous catalysts,[17-20] transition metal compounds (phosphides,[21-26] carbides,[24, 25] and nitrides[25, 27]), but mainly noble metals (Pt, Pd, Rh, Ru),[14, 15] have been used, but these require high temperature, and high pressure conditions. For example, Lu et al showed Pd/TiO_2 catalyses with the HDO/hydrogenation of guaiacol to cyclohexane, but this required 30 bar H_2 at 260 ℃.[28] Kim et al. reported that ruthenium on carbon (Ru/C) converted guaiacol to cyclohexanol with 60% selectivity using the H-donor 2-propanol without added H_2 at 200 ℃ for 5 h, but the HDO was only partial.[29]

The use of Niobium Oxide has primarily been studied to show its specific role involved in HDO. Shown in the studies of Wang et al., Nb_2O_5 was primarily used as a catalyst support for Ruthenium to form indane with and without the addition of CH_2Cl_2 as its primary solvent. The main function Nb_2O_5 partook was catalysing the intramolecular cyclization and hydrogenation of lignin oil.[7] Jiang et

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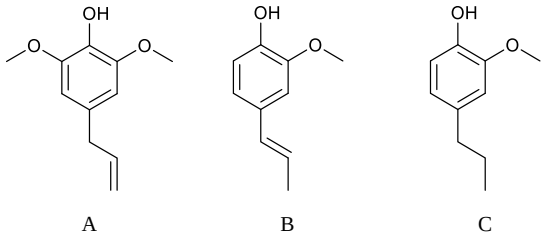


Figure 1. Structures of lignin monomer compounds: (A) 4-allyl-2,6-dimethoxyphenol (4-allysyringol), (B) isoeugenol, (C) 2-methoxy-4-propylphenol (dihydroeugenol, DHE)

al., utilized Ni/Nb_2O_5 catalyst to produce value-added alcohols from lignin-derived phenols which exhibited selective HDO to give a total alcohol yield of 74%, but requires higher pressure (25 bar H_2).[8] Puurunen et al., used Pt/Nb_2O_5 to perform HDO on lignin monomer, 4-propylphenol under harsh temperature and pressure (350 °C, 20 bar H_2) to give a selectivity of 77% propylbenze.[9] Rinaldi et al., studied Ni/Nb_2O_5 by tuning the acidic and hydrogenating properties of the catalyst to convert lignin to hydrocarbons at 91% yield under 15% catalyst loading and harsh conditions (200°C, 40 bar H_2).[30] Yang et al., reported Nb_2O_5 supported for Pd and Pt where they concluded HDO conversion of lignin to C_7-C_9 products at 42 and 64%, respectively.[18]

Described here is the hydroprocessing of dihydroeugenol (DHE) in an aqueous medium using a physical mixture of two catalysts acting synergistically, one is Ru/C, the other is niobium pentoxide (Nb_2O_5). DHE was used as the primary model compound for testing the present catalytic system, since it includes the methoxy, hydroxy, and a propyl groups characteristic of the lignin monomers present in bio-oils (Figure 1). Nb_2O_5 is an air stable, water insoluble white solid that exhibits both strong Lewis and Brønsted acid sites.[31] It has proved to be an effective catalyst for hydration/dehydration, cracking, condensation, isomerization, and alkylation[32-35] as well as for HDO.[32-34, 36]

The dual catalyst system is effective in hydroprocessing DHE and several other lignin monomers under relatively mild conditions to produce hydrocarbons in high yields. We find that addition of small quantities of methanol (MeOH) as a co-reactant has a significant influence on the product distribution and offer evidence-based mechanistic insight. Furthermore, this system can be tuned to give high selectivity towards hydrocarbon products that can be employed as drop-in fuels.

Experimental

Regents and Feedstocks

All commercial chemicals were purchased and used as received. 2-Methoxy-4-propylphenol (≥99%), isoeugenol (98%), 2,2-biphenol (99%), and niobium(V) oxide (325 mesh, 99.9%) were purchased from Sigma-Aldrich. Dichloromethane (ACS reagent grade), methanol (ACS Reagent Grade), ethanol (200 Proof), and ethyl acetate (ACS Reagent Grade) were purchased from Fisher Chemical. Cetyltrimethyl ammonium bromide (CTAB, 98%) and n-dodecane (99%) were purchased from Alfa Aesar. Deuterium oxide (D, 99.9%), and methanol-d_4 (D, 99.8%) were purchased from Cambridge Isotope Laboratories Inc. Propyl benzene (98%) was purchased from Frontier Scientific. Para-cresol (cresylic acid) was purchased from Hercules Powder Company. Hydrochloric Acid (GR ACS) was purchased from EMD Millipore Corporation. Niobium (V) chloride (≥99%) was purchased from Strem Chemicals. Hydrogen gas (5.0 grade) and nitrogen (99.998%) were purchased from Praxair. Water used for reaction and sample preparation was obtained from a A10 Milli-Q water purification system by Millipore.

Catalyst Preparation

Ru/C was obtained from Sigma-Aldrich with 5 wt% Ru loading and used as received. Nb_2O_5 was synthesized using a hydrothermal method according to a modified literature procedure.[35] Typically, a 20 mmol portion of the precursor $NbCl_5$ was dissolved in 20 mL ethanol with rigorous stirring for 10 min, then the solution was added to water solution of CTAB (1 g in 15 mL distilled water) dropwise. The mixed solution was then stirred for 0.5 h followed by adding 20 mL of aqueous HCl (pH 1) that was previously prepared by dissolving a specific amount of hydrochloric acid in water and stirring for another 1.5 h. The resulting sol was then put into a Teflon-lined autoclave and aged at 160 ℃ for 24 h. Subsequently, the solid was separated and washed with distilled water and dried at 60 ℃ overnight. After that, the sample was ground and packed for calcination in air. A Thermolyne F6020 1200C Muffle furnace was used to calcinate the niobia sample. Ramping rate of the furnace was pre-set to 1 ℃/min. After 6h calcination at 450℃, the active Nb_2O_5 catalyst was collected at room temperature.

Catalyst Characterization

***NH_3-Temperature Programmed Desorption (TPD)*:** To evaluate the acid sites on Nb_2O_5, NH_3-TPD was performed on a Micromeritics AutoChem 2920 instrument. A 200 mg sample of Nb_2O_5 was placed into a U-shaped quartz tube. This material was first pretreated by heating under flowing helium (25 cm^3/min) at 300 ℃ for 0.5 h. A mixture of NH_3 in He (1:9 v/v) was then passed through the tube at a flow rate of 15 cm^3/min at 25 ℃ for 1 h. After that, the sample was flushed with He (25 cm^3/min) at 100 ℃ for another hour. The TPD measurements were carried out over the temperature range 100-500 ℃ at ramp rate of 10 ℃ /min and the ammonia concentration in the effluent was monitored with filament thermal conductivity detector (TCD). The amount of desorbed ammonia was determined based on the integrated peak area.

X-ray Diffraction (XRD): The phase structure of Nb_2O_5 was analyzed by powder X-ray diffraction in the diffraction angle 2θ between 10° and 80° on a PANalytical X'Pert PRO X-ray diffractometer with Cu Kα1 radiation (45 kV and 40 mA, k = 1.5406 Å).

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM): The particle size and micro morphology of Nb_2O_5 were characterized by scanning electron microscopy (Hitachi SU-8010) at an acceleration voltage of 15

kV. The pore structure of Nb_2O_5 was examined using high-resolution transmission electron microscopy (Tecnai G2 F20 S-TWIN) with the acceleration voltage of 200 kV.

X-ray Photoelectron Spectroscopy (XPS): The niobium oxidation state in the synthesized Nb_2O_5 catalyst was analyzed by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha+, USA) with a monochromatic radiation source Al Kα (12kV, 6mA, 72W). The wide scans were performed with 100 eV pass energy and 1 eV energy step, and the high resolution scans were performed with 30 eV pass energy and 0.1 eV step size. The C1s signal of adventitious carbon (284.8 eV) was used for energy calibration.

Catalytic reaction and product analysis

Reactions in Parr reactor: Batch reactions were carried out in a stainless steel 75 mL 6-series pressure reactor (Parr Instrument Company, 5000 series). The reactor vessel was equipped with magnetic stirring system. For a typical reaction, 0.1 g Ru/C and 0.2 g Nb_2O_5 were physically mixed in the vessel with 12 mL distilled water as solvent. To this were added substrate (0.2 mL) and MeOH (0.8 mL). The reactor was then sealed and purged with H_2 three times. Then, the reactor was filled with H_2 (6 bar). The reactor was heated to 250 ℃ and held at that temperature for a defined time (typically for 12 h). The stirring rate was kept at 700 rpm during the whole reaction period. Subsequently, the reactor was cooled to room temperature. The products in the liquid phase were extracted using ethyl acetate and the gas phase products were collected in a sealed gasbag for further analysis.

Catalyst Recyclability Test: The recycle experiments were performed in five successive runs with 1 mL DHE loading of each. A physical mixture of fresh Ru/C (0.1 g) and Nb_2O_5 (0.2 g) was employed in the first run. MeOH (1 mL) was then added with 12 mL distilled water as solvent to the reaction mixture in a 75 mL reactor vessel. The reactor was sealed and purged with H_2 three times. Then, the reactor was filled with 11 bar H_2 at room temperature. After that, the reactor was heated to 250 ℃ and held for 16 h with magnetic stirring at 700 rpm. After reaction, products in liquid phase were extracted using ethyl acetate. The catalyst was washed using ethanol and collected by centrifugation, then dried in a vacuum chamber for 24 h at room temperature. Prior to the next recycle run, the catalyst mixture was heated in an oven at 120 ℃ for 1 h. The following runs were performed with the same portion of this catalyst mixture collected from the previous run. Turnover number (TON) of each catalyst was calculated based on the total amount of C9 hydrocarbons, i.e. propyl benzene and propyl cyclohexane, produced after the fifth run to show the productivity of each catalyst. The TON was defined and calculated as follows:

$$TON = \frac{total\ moles\ of\ C9\ hydrocarbons\ by\ 5\ runs}{moles\ of\ catalyst}$$

GC-MS Analysis: A Hewlett-Packard 5890A gas chromatograph (GC) coupled to a Hewlett-Packard 5970B Mass Selective Detector (MSD) was used to identify the products qualitatively. A J&W DB-5 capillary column (30 m x 0.250 mm I.D. x 0.25 μm film thickness) was installed for analyte separation. Prior to the injection, the liquid sample was dissolved in ethyl acetate and filtered through a 0.2 micron PTFE syringe filter. The GC injector inlet was set to 280 ℃. The oven temperature was held at 50 ℃ for 2 min. Then the oven was heated to 300 ℃ at rate of 20 ℃ per min and held for 10 min. The MSD had a dedicated electron ionization (EI) source and a quadrupole mass analyzer. The mass range of detection was 40 to 550 m/z at a rate of 1.6 scans per second.

GC-FID Analysis: An Agilent 6890N gas chromatograph equipped with a flame ionization detector (FID) was used to quantify the reaction mixtures. A J&W DB-5 GC column (30 m x 0.250 mm I.D. x 0.25 μm film thickness) was selectively used for separation. The liquid products sample was first passed through a 0.2 micron PTFE syringe filter to remove solid particles, and then diluted to 25 mL in a volumetric flask. A 10 mM n-dodecane solution was pre-made as internal standard for GC quantification. The sample solution was mixed with internal standard (1:1 v/v) in a 2 mL Agilent GC vial. The sample was injected by autosampler. The inlet temperature was kept at 280 ℃ while the detector temperature was 310 ℃. The initial temperature of oven was 40 ℃ and held for 7 min. Then the oven was heated to 250 ℃ at ramp rate of 10 ℃/min and kept at the final temperature for 5 min. The split mode was used with the split ratio of 10:1. Helium was used as carrier gas at flow rate of 14 mL/min. The instrument was calibrated using the known samples of the products. The analytes were then identified according to their retention time. The quantification of each analyte was acquired from a calibration curve which represented the relationship between concentration versus the ratio of peak area over internal standard.

GC-TCD Analysis: Gas phase products were analyzed by GC-TCD. An Agilent 6890N (G1530N) gas chromatograph equipped with a thermal conductivity detector (TCD) and 30 m × 0.53 mm Fused Silica Carboxen 1010 capillary column was used. The detector was set to 250 ℃ with H_2 flow at 7 mL/min and air flow at 8 mL/min. The gas phase products were collected in RESTEK polypropylene combo valve gas sampling bag. For each measurement, the 50 μL gas sample was manually injected by a gastight syringe into the GC inlet at 245 ℃. The carrier gas, He, was set to 7 mL/min. The column was pre-heated to 35 ℃ and held for 5 min. Then the temperature ramped to 245 ℃ at the rate of 10 ℃/min and held for 10 min. Each gas analyte was identified by its retention time.

NMR Analysis: ^{1}H NMR was obtained by Varian Unity Inova 600 MHz spectrometer. The analyte was extracted by 700 μL $CDCl_3$ and packed in glass NMR tube for analysis. ^{2}H NMR was done by using Agilent 400-MR DDR2 400 MHz spectrometer. $CHCl_3$ with 10% $CDCl_3$ internal standard was used as the solvent for ^{2}H NMR analysis.

Results

Optimization of dihydroeugenol (DHE) hydrodeoxygenation:

A typical HDO run involved heating a mixture of the model substrate DHE (0.20 mL) with the catalysts Ru/C (100 mg) and Nb_2O_5 (200 mg) added separately, water (12 mL) and a small

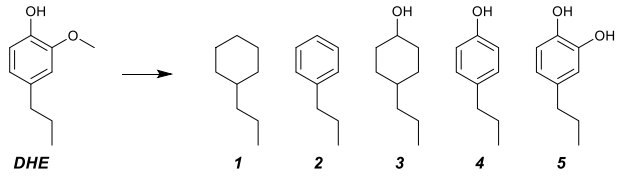


Figure 2. DHE Conversion into five main products: propyl cyclohexane (1), propyl benzene (2), 4-propylcyclohexan-1-ol (3), 4-propylpheol (4), and 4-propylcatechol (5).

amount of MeOH (0.8 mL) in a closed Parr® high pressure re actor that had been flushed with H_2 ($P(H_2)$ = 1 atm at room temperature, RT) then sealed. After a 12 h reaction at 250 ℃, the conversion of DHE was 95% (entry 3, Table 1) and of the five potential products shown in Figure 2, the fully deoxygenated hydrocarbons propyl cyclohexane (**1**) and propyl benzene (**2**) made up 64% of the product mixture. The balance was mostly the partially deoxygenated product 4-propylcyclohexanol (**3**). Thus, this catalyst mixture is a promising HDO system. The studies described here were designed to examine the effects of key variables such as MeOH concentration, H_2 pressure, and catalyst loading in order to define those features that may give the optimum selectivity toward desired product streams.

Table 1. Performance comparison with different amounts of methanol.

Entry	MeOH (mL)	Conv. (%)	Product Distribution (%)				
			1	**2**	**3**	**4**	**5**
1[a]	0	82	3.3	3.5	80	13	-
2[b]	0.4	80	3.6	9.5	42	45	-
3[b]	0.8	95	42	22	34	2	-
4[b]	4	36	8	10	-	24	58
5[c]	0	0	-	-	-	-	-

Common conditions for each reaction: DHE 0.2 mL, Ru/C 100 mg, Nb_2O_5 200 mg, H_2O 12 mL, 250 ℃, 12 h. Unless noted otherwise, the reactor was first flushed with H_2. [a] Initial $P(H_2)$ at RT = 6 bar (5 bar, gauge). [b] Initial $P(H_2)$ at RT = 1 bar. [C] Purged with nitrogen, no added H_2.

Table 1 illustrates the remarkable sensitivity of this system to the amount of methanol added as well as the cooperative requirement for both MeOH and H_2 to obtain the desired HDO products (**1**) and (**2**). For example, the reaction with no MeOH but with $P(H_2)$ = 6 bar (RT) (entry 1, Table 1) gave substantial conversion of DHE, but only ~7% of the fully deoxygenated hydrocarbons. In the absence of both H_2 and MeOH, no conversion was observed, and no products were detected (entry 5, Table1).

Entries 2-4 in Table 1 compare the effect of changing the amount of MeOH added while holding $P(H_2)$ constant at 1 bar (RT). Under these conditions, the optimum amount of MeOH proved to be 0.8 mL. Surprisingly, raising the MeOH to 4 mL, only about one third the quantity of the aqueous cosolvent, suppressed both the conversion of DHE and the relative amount of HDO products.

Table 2 summarizes the product distributions found for DHE reactions for various $P(H_2)$ (RT) under typical conditions with 0.8 mL MeOH. In the absence of any externally added H_2 (entry 1, Table 2) there was about 64% conversion of DHE, but the only products were the phenol and cyclohexanol derivatives (**4**) and (**3**). The amount of conversion increases under increasing H_2 and is 100% when $P(H_2)$ is 6 bar or greater (entries 4-5, Table 2). More importantly, the yield of propyl cyclohexane (**1**) is 100%. Thus, the latter result requires addition of both MeOH and H_2 and the distribution of HDO products is a function of $P(H_2)$ with high selectivity occurring at a relatively low $P(H_2)$.

Table 2. Performance with different hydrogen pressures

Entry	$P(H_2)$ in bar [a]	Conv. (%)	Product Distribution (%)				
			1	**2**	**3**	**4**	**5**
1[b]	0	64	-	-	31	69	-
2[c]	1	95	42	22	34	2	-
3	2	98	53	17	27	3	-
4	6	100	100	-	-	-	-
5	11	100	100	-	-	-	-

Common conditions for each reaction: DHE 0.2 mL, Ru/C 100 mg, Nb_2O_5 200 mg, H_2O 12 mL, MeOH 0.8 mL, 250 ℃, 12 h. Unless noted otherwise, the reactor was first flushed with H_2. [a] Initial $P(H_2)$ at RT. [b] Reactor purged with N_2 only, $P(N_2)$ = 1 atm at RT. [c] The same experiment as entry 3 in Table 1.

Table 3 summarizes experiments with different catalyst mixtures. Interestingly, when the reaction was examined with the addition of Nb_2O_5 alone, the material prepared in this laboratory proved to be much more active than that purchased from a commercial source. The XRD pattern, XPS analysis, SEM and TEM images of the synthesized Nb_2O_5 showed it to be an amorphous, mesoporous catalyst with the niobium in the +5 oxidation state (Supporting information (SI) Figures S-1 and S-2).

The principal reaction in the former case was hydrolysis of the DHE methoxy group to give catechol (**5**) (entry 1, Table 3) while little activity was seen with the commercial Nb_2O_5 (entry

Table 3. Performance with different catalyst mixtures

Entry	Ru/C (mg)	Nb_2O_5 (mg)	Conv. (%)	Product Distribution (%)					P_{final} (bar)
				1	**2**	**3**	**4**	**5**	
1[a]	0	200	80	-	-	-	4	96	6
2[b]	0	200	-	-	-	-	-	-	6
3	100	0	96	7.7	8.2	82	2.1	-	14.5
4[c]	100	0	100	72	-	28	-	-	11.6
5[a, d]	100	200	100	100	-	-	-	-	11

Reaction condition: DHE 0.2 mL, H_2O 12 mL, methanol 0.8 mL, $P(H_2)$ = 6 bar, 250 ℃, 12 h. [a] Nb_2O_5 was custom prepared in this laboratory as described in the Experimental section. [b] commercial Nb_2O_5 calcined at 1000 ℃. [c] Ru/C was pre-treated in 12 mL H_2O under 10 bar H_2 at 200 ℃ for 2 h. [d] The same reaction as entry 4 in Table 2.

2, Table 3). One possible explanation may lie in the manner in which the two Nb_2O_5 samples were processed. The commercial sample had been calcined at 1000 ℃ while the Nb_2O_5 sample prepared in our laboratories and used for catalysis was calcined at 450 ℃ . Accordingly, we speculated that the higher temperature calcination may have diminished the number of acid sites on Nb_2O_5. This idea was tested by TPD studies of Nb_2O_5 samples that had been first dried and then exposed to ammonia. The amount of NH_3 was absorbed by the Nb_2O_5 sample calcined at 450 ℃ was 28 mmol per gram of Nb_2O_5 while an analogous sample prepared in this laboratory but calcined at 600 ℃ only absorbed and released about 2 mmol NH_3 per gram of the sample (SI Figure S-3). Furthermore, the commercial sample absorbed and desorbed essentially no NH_3. Thus, it is clear that higher temperature calcination strongly diminishes the number of acid sites on Nb_2O_5.

When Ru/C alone was used as a catalyst without pretreatment, the major product was propylcyclohexanol (**3**) although about only 8% each of the hydrocarbons (**1**) & (**2**) were formed (entry 3, Table 3). When the Ru/C was first pre-treated by heating under hydrogen to 200 ℃, the observed reactivity changed. The major product was propylcyclohexane (**1**) (72%) with the cyclohexanol (**3**) being the remainder (28%) (entry 4, Table 3). Unde r analogous conditions, the system to which both Ru/C (not activated with H_2) and Nb_2O_5 had been added gave 100% conversion to the propylcyclohexane product exclusively (entry 5, Table 3). Notably, when either form of Ru/C was present, the final pressure in the Parr reactor (after cooling to RT) was significantly higher than the initial $P(H_2)$. This is apparently due to catalytic reforming of MeOH.

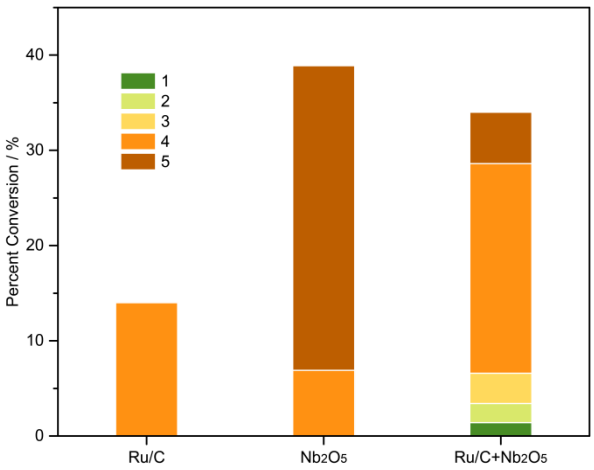
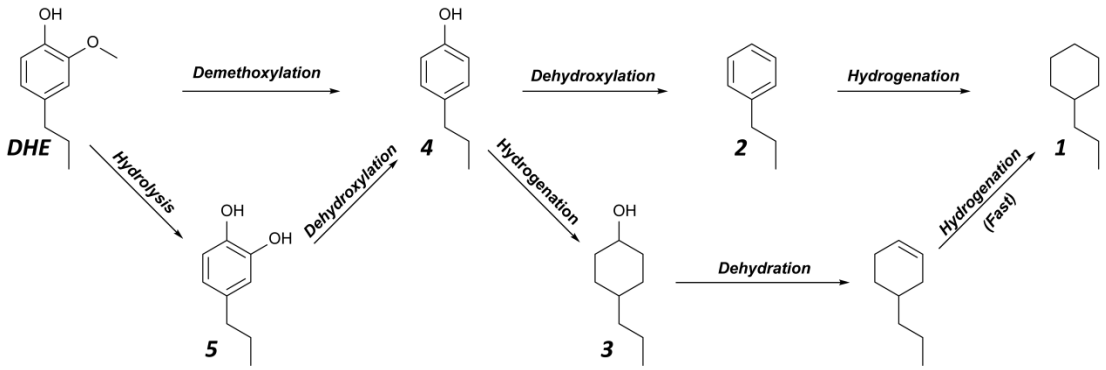


Figure 3. Graphic showing conversion (vertical axis) and product distribution after a 2 h reaction for a mixture of DHE (0.2 mL), H_2O (12 mL), MeOH (0.8 mL) under H_2 (6 bar) with Ru/C (100 mg), Nb_2O_5 (200 mg) or both at 250 ℃.

Thus, H_2-pretreated Ru/C can catalyse the HDO/ hydrogenation of DHE, although the reaction is more efficient when Nb_2O_5 is present. On the other hand, low T calcined Nb_2O_5 alone only catalysed the conversion of DHE to the



Scheme 1. Possible sequence of reactions leading from DHE to (1).

Table 4. Reaction performance in different isotopically labelled reactants

Entry	Water	Methanol	Hydrogen	Conv. (%)	Product Distribution (%)					P_{final} (bar)
					1	**2**	**3**	**4**	**5**	
1[a, b]	H_2O	MeOH	H_2 (1 bar)	80	3.6	9.5	42	45	-	8
2[b]	H_2O	MeOH	H_2 (1 bar)	95	42	22	34	2	-	11
3	D_2O	methanol-d_4	H_2 (1 bar)	54	-	-	-	66	34	6
4[c]	D_2O	methanol-d_4	H_2 (1 bar)	85	2.5	5.4	48	44	-	9.7
5	D_2O	MeOH	H_2 (1 bar)	81	1	3.1	11	82	2.3	9.1
6[b]	H_2O	MeOH	H_2 (6 bar)	100	100	-	-	-	-	11
7[d]	D_2O	methanol-d_4	H_2 (6 bar)	100	94	0.1	6.2	-	-	8.9
8	H_2O	MeOH	D_2 (6 bar)	100	61	21	16	2	-	9.6

Conditions: DHE 0.2 mL, Ru/C 100 mg, Nb_2O_5 200 mg, water 12 mL, methanol 0.8 mL unless noted, purged with H_2 and vented to give $P(H_2)$ = 1 bar, unless noted, 250 °C, 12 h reaction time, unless noted. [a] Methanol 0.4 mL.[b] Entry 1 and entry 2 are the same reactions as entry 2 and entry 3 in Table 1; entry 6 is the same reaction as entry 4 in Table 2. [c] Reaction time 24 h. [d] $P(H_2)$ = 6 bar.

catechol (**5**), presumably the product of hydrolysis of the methoxy group.

The observation that the Ru/C catalyst is more active after pre-treatment suggested that the early stages of the reactions with the physically mixed catalyst would show an induction period while the Ru/C was being activated. This suggestion led to the experiments reported in Figure 3 and SI Table S-1 to examine the products formed by different catalyst combinations over an initial period of 2 h. The take-home lesson from Figure 3 is that, on this time scale, Ru/C alone displays modest activity (14% conversion), but the only product observed was the phenol (**4**), the result of HDO removal of the DHE methoxy group. With Nb_2O_5 alone, conversion was considerably higher, but the primary product was the catechol (**5**). The result with both catalysts illustrates the synergy of this mixture. Although the conversion was about the same as seen with Nb_2O_5 alone, products (**1**), (**2**) and (**3**) are also evident. Scheme 1 suggests a possible sequence of these transformations, with a principal role of the Nb_2O_5 being to catalyse the hydrolysis of the DHE methoxy group to form the catechol (**5**), although, surprisingly, a small amount of the phenol (**4**) was still formed with Nb_2O_5 alone.

Figure 4 illustrates the behaviour of the mixed catalyst system as a function of reaction time. These data confirm the suspected induction period, during which the Ru/C catalyst is activated. After 4 h, all the DHE had been converted to products with 2/3 of the total being the hydrocarbons (**1**) & (**2**). By 8 h, all the products were (**1**) & (**2**) with propyl cyclohexane (**1**) representing an impressive 94 %, while after 12 h only a single product, (**1**), was evident (SI Table S-1). Formation of (**1**) requires HDO of both oxygen containing functional groups of DHE and the hydrogenation of the aromatic ring. Notably, the cyclohexanol (**3**) is observed as an intermediate that presumably undergoes HDO, but none of the direct product of DHE ring-hydrogenation 4 -propyl-2-methoxy-cyclohexanol was evident.

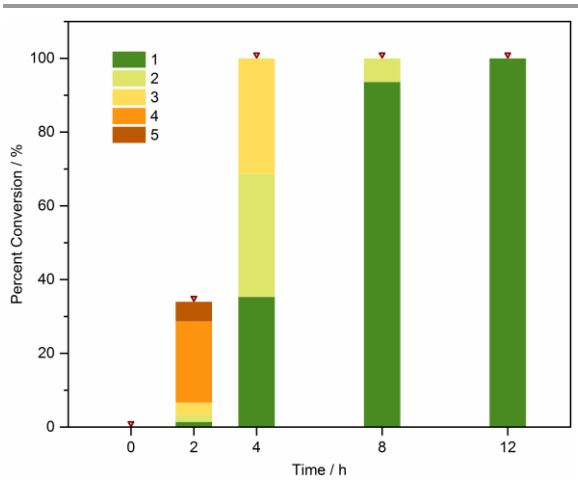


Figure 4. Graphic showing conversion (vertical axis) and product distribution after from 2h, 4h, 8h, 12h reaction for a mixture of DHE (0.2 mL), H_2O (12 mL), MeOH (0.8 mL) under H_2 (6 bar) with Ru/C (100 mg) and Nb_2O_5 (200 mg) at 250 °C.

Reactions of DHE with deuterated reactants

Table 4 summarizes the conversion and products from analogous reactions of DHE in deuterated solvents. Notably, when both D_2O and methanol-d_4 were used instead of the perprotio analogues, there was a significant suppression both of the conversion and of the formation of the more reduced products (**1**), (**2**) and (**3**) with only (**4**) and (**5**) being found (entry 3, Table 4). Extending the reaction time to 24 h did increase production of (**1**), (**2**) & (**3**) with the cyclohexanol (**3**) and the phenol (**4**) now being the major products (entry 4, Table 4). The

pattern was again different when the solvent mixture was D_2O with perprotio MeOH (entry 5, Table 4). The conversion was greater (81%) than when methanol-d4 was used (54%), and measurable amounts of (**1**), (**2**) & (**3**) were found, but the primary product was (**4**). Thus, isotope effects are evident in the product distributions from the deuteration of each solvent.

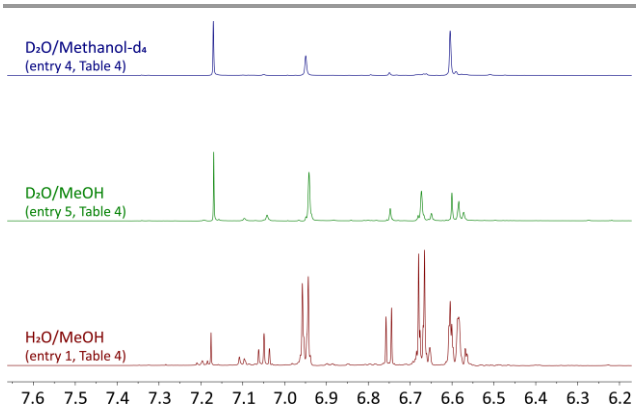


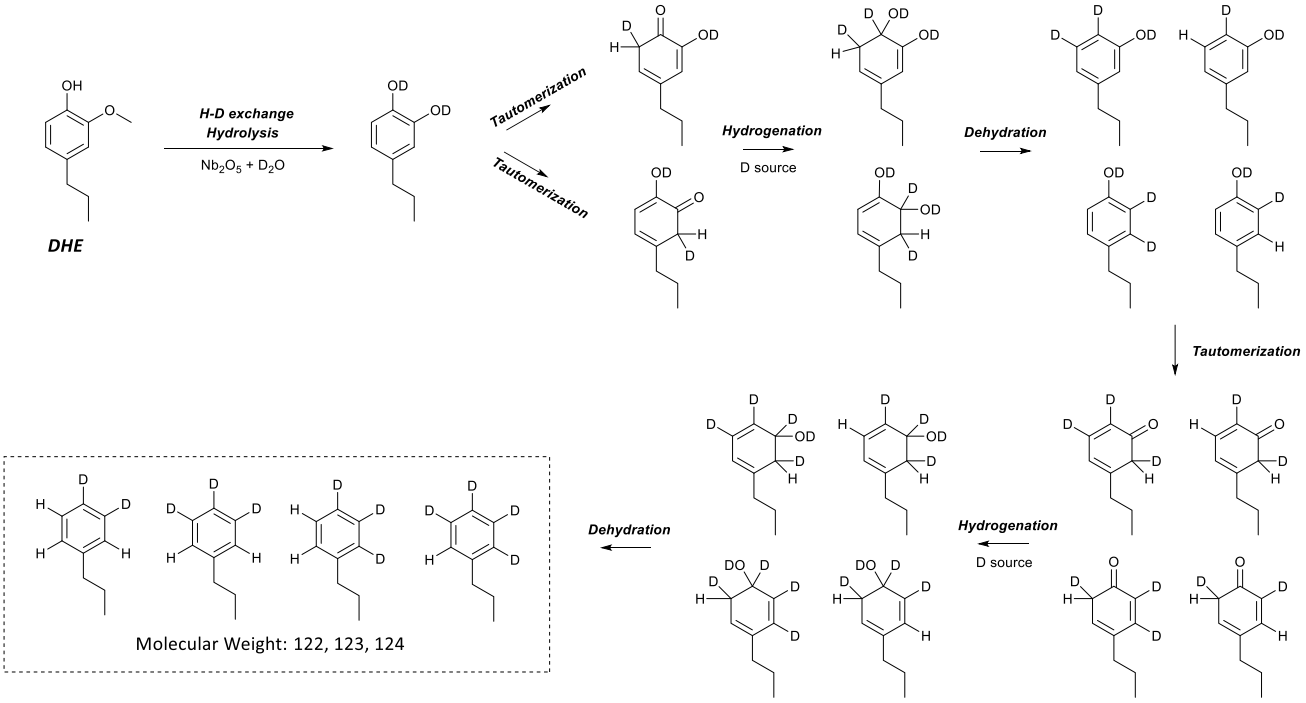
Figure 5. ^1H NMR in the aromatic region of the products obtained after DHE reactions in D_2O/methanol-d_4 (top, entry 4 in Table 4) D_2O/MeOH (middle, entry 5 in Table 4) and H_2O/MeOH (bottom, entry 1 in Table 4)

The DHE reaction with the two catalysts was also run in the D_2O/methanol-d_4 solvent with a higher P(H_2) of 6 bar (entry 7, Table 4). As observed above (entry 6, Table 4), raising the hydrogen pressure substantially accelerated the reaction and improved the selectivity toward (**1**) to 94% in the deuterated medium.

Figure 5 displays the aromatic regions of the ^1H NMR spectra of products isolated after reactions in H_2O/MeOH (entry 1, Table 4), D_2O/methanol-d4 (entry 4, Table 4) and D_2O/MeOH (entry 5, Table 4). SI Figure S-4 displays the aliphatic regions of these spectra. A particularly meaningful comparison is between the spectra of entries 1 and 4 in Table 4 since the product distributions for these are very similar with (**4**) being the primary aromatic product in each case. Simple inspection of these spectra shows that considerable exchange of the aromatic protons with the solvents accompanies the transformation of DHE to the phenolic product (**4**). Their similar patterns in the aliphatic region indicate the deuterated reactants and solvent have little influence on the exchange of alkyl protons. The ^2H NMR spectrum of the product mixture from entry 4 in Table 4 confirms the introduction of both aromatic and aliphatic hydrogens from the deuterated solvent (SI Figure S-5).

The same conclusion can be drawn from the mass spectrum (obtained by GC-MS analysis) of product (**2**) formed by reaction in D_2O/methanol-d_4 (entry 4, Table 4). The parent MS peak for propylbenzene should appear at mass 120, but the major peak in this region of the MS spectrum (SI Figure S-6) appeared at M /e 123, again indicating that H/D exchange of the aromatic ring occurred prior to ring hydrogenation. Scheme 2 offers a plausible pathway for such exchange via tautomerization of the catechol product (**4**) formed by hydrolysis of the DHE methoxy group.

The proposed catechol tautomerization mechanism was tested by carrying out the reaction of p-cresol with Nb_2O_5 with D_2O under 6 bar H_2 at 250 °C for 12 h. No HDO of this substrate was observed, but inspection of the aromatic region ^2H NMR and mass spectrum of the recovered p-cresol (SI Figure S-7)



Scheme 2. Hypothetical pathways for exchange of aromatic protons with solvent. H-D exchange reaction is very fast in water.

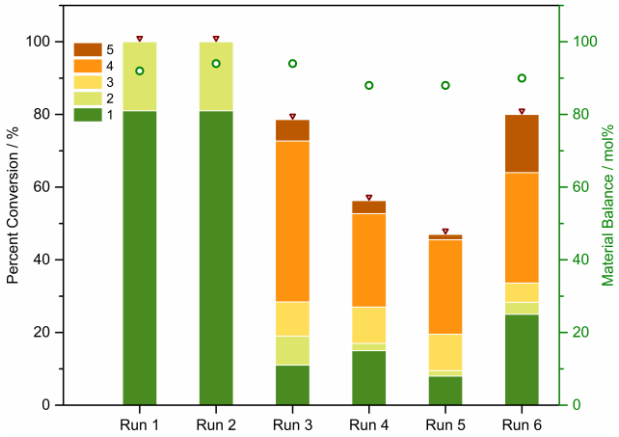
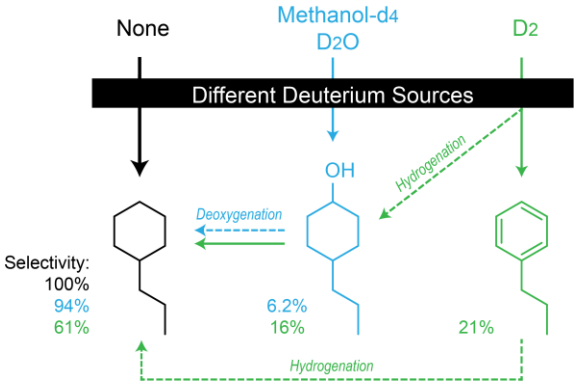


Figure 6. Performance of catalyst reusability. The catalyst mixture was washed twice using ethanol, dried in vacuum chamber at RT for 24 h, and heated in oven at 120 °C for 1 h prior to the next run. For Run 4, catalyst was calcinated under N_2 at 450 °C for another 45 min before use. For Run 5, catalyst was reduced under H_2 (5 %)/Ar at 350 °C for 3 h before use. For run 6, fresh Nb_2O_5 0.1 g was added to the recovered catalyst (0.2 g remained after run 5). The height of the bar represents the amount of conversion while the small circle represents the material balance of recovered reactant and products which averaged ~91% after workup.

showed that there had been considerable hydrogen exchange with the solvent, as would be expected via tautomerization as illustrated in Scheme 2.

Table 4 also lists the DHE reaction run with the two catalysts in the H_2O/MeOH solvent with D_2 at a pressure of 6 bar (entry 8, Table 4). In this case, the yield of (**1**) was only 61% as opposed to the 100% selectivity seen under comparable conditions with H_2 (entry 6, Table 4). Products (**2**) (21%) and (**3**) (16%) made up the bulk of the other products. Thus, there is a substantial kinetic isotope effect on the HDO and aromatic ring reduction reactions upon replacing H_2 with D_2. The ^2H NMR spectrum of the product mixture shows deuterium in the aliphatic region corresponding to (**1**) and (**3**) and no deuterium in the aromatic region (SI Figure S-8), consistent with dihydrogen (H_2/D_2) as the source of aromatic hydrogenation. Scheme 3 outlines the various pathways indicated by these isotope effects.



Scheme 3. The apparent roles of different hydrogen sources.

Catalysis recyclability and stability test

The recyclability of the Ru/C and Nb_2O_5 mixture for DHE conversion was tested in five successive runs (Figure 6 and SI Table S-2). An optimized reaction condition with higher substrate loading (1 mL DHE) and longer reaction time (16 h) was applied to understand the performance of this catalyst mixture. Within the first two runs, 12.5 mmol DHE was fully converted to products (**1**) (81%) and (**2**) (19%) (Runs 1 and 2, Figure 6 and SI Table S-2). The conversion of DHE decreased significantly to 78.6%, for run 3. Attempts to reactivate the catalyst mixture by calcining at 450 °C (run 4) or heating under H_2 (run 5) were unsuccessful with conversion dropping to 56%, and 47%, respectively. Thus, the catalyst mixture became less active toward HDO reactions after the second recycle given that propyl phenol (**4**) was the main product in the last three runs. Overall, the catalyst mixture was able to catalyse 15.06 mmol DHE to fully deoxygenated products (**1**) and (**2**) during the first five runs. Notably, the addition of fresh Nb_2O_5 (0.1 g) led to a marked increase in conversion (80%) and yield of hydrocarbon products. For the six runs the material balance of recovered reactant and products averaged 91±3 mol%.

The calculated TON for hydrocarbon production for the first 5 runs was 301 based on the ruthenium (0.05 mmol) or 20 based on the Nb_2O_5 (0.75 mmol) initially present.

Application to a mixture of lignin monomers.

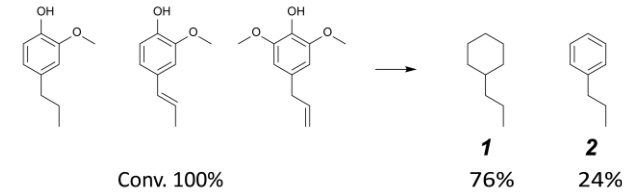
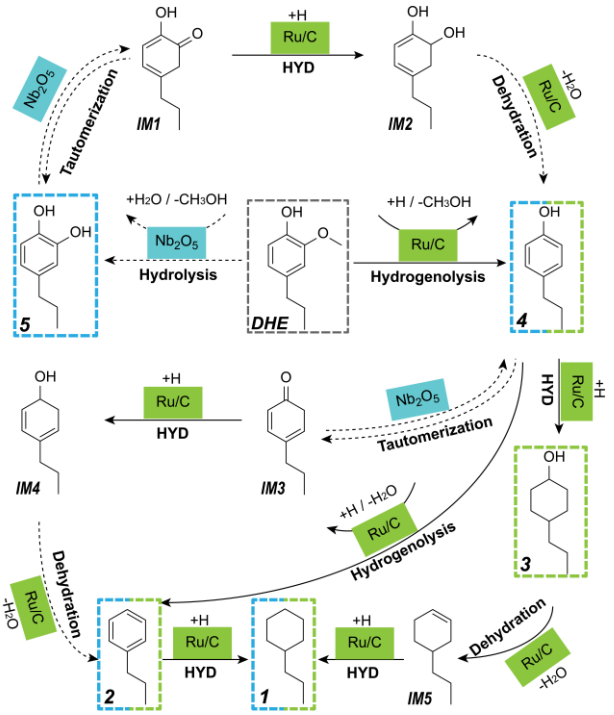


Figure 7. The reaction with a mixture of monolignols: dihydoeugenol (DHE), isoeugenol and 4-allylsyringol. Conditions: 70 µL of each substrate, Ru/C (100 mg), Nb_2O_5 (200 mg), H_2O (12 mL), MeOH (1.2 mL), P(H_2) = 11 bar, 250 °C, 12 h reaction time.

DHE, isoeugenol, and 4-allylsyringol are among the most common lignin monomers. When a mixture of these three substrates (70 µL of each) was subjected to the standard procedure for 12 h, the only products were the hydrocarbons (**1**) (76%) and (**2**) (24%) according to GC analysis (Figure 7). Since a 100% yield of (**1**) can be achieved with an extended reaction time, this system offers a viable new strategy for funnelling the multiple monolignols from lignin disassembly into a much simpler mixture of C9 alkanes.



Scheme 4. A proposed sequence of mechanistic steps for conversion of DHE by the catalyst mixture Ru/C and Nb_2O_5 in a H_2O/MeOH medium under H_2. Hydrogenation is abbreviated as "HYD".

Discussion

Reported are batch reactor studies addressing the hydrodeoxygenation (HDO) of the lignin monomer dihydroeugenol to the hydrocarbons propyl cyclohexane (**1**) and propyl benzene (**2**). This transformation is affected by a Ru/C and Nb_2O_5 co-catalyst mixture under H_2 in an aqueous medium containing a small amount of methanol additive. The key observations are:

(a) MeOH serves as a secondary hydrogen donor that promotes HDO under lower H_2 pressures compared to current methods.[37-41] The overall reaction appears optimal with a H_2O/MeOH ratio ~15 and H_2 pressures of 1-6 bar. The increased pressure after the reaction and the presence of CO_2 in the gas phase (SI Figure S-9) are consistent with methanol being reformed in the presence of Ru/C.

(b) The Nb_2O_5 is primarily active in the conversion of DHE to 4-propylcatechol (**5**), presumably by hydrolysis of the methoxy group.[42] The Nb_2O_5 prepared in this laboratory and calcined at 450 °C was much more active than a commercial sample that was apparently calcined at a much higher temperature.[43] The difference was attributed to the much greater number of acid sites on the former material as shown by NH_3-TPD test (Figure S-1).[44]

(c) Ru/C catalyses HDO of (**5**) and the subsequently formed intermediates 4-propylcyclohexan-1-ol (**3**) and 4-propylphenol (**4**), and hydrogenation of the aromatic ring.[45, 46] The Ru/C is more effective after pre-treatment by heating under H_2. While Ru/C alone can catalyse HDO of DHE to products (**1**)-(**4**), the synergistic activity of the two-catalyst system is more efficient and selective, toward as much as 100% conversion and selectivity to propylcyclohexane (**1**).

Scheme 4 outlines the likely sequence of catalysed reactions leading to the potential products. Conversion of DHE is initiated into two pathways by each catalyst. The proposed mechanism of Ru/C catalysed HDO is, highlighted in green colour with solid arrows in Scheme 4). This is based on the observed production of (**1**)-(**4**) with Ru/C alone (Entries 3 and 4, Table 3, and Figure 4). The deoxygenated products can be obtained through hydrogenolysis, dehydration, and hydrogenation reactions.

The reactions labelled with dash lines and blue colour in Scheme 4 describe proposed pathways via intermediates (**IM1**)-(**IM4**) facilitated by activated Nb_2O_5 and based upon the observations of 4-propylcatechol (**5**) formation in the initial stage (entry 1, Table 3, and Figure 3). Key steps in this mechanism are Nb_2O_5 catalysed tautomerizations of (**4**) and (**5**) to give carbonyl species (**IM1** & **IM3**) followed by activated Ru/C catalysed hydrogenation to give a cyclic diene alcohols (**IM2**, **IM4**), that upon dehydration are rearomatized to (**2**) and (**4**), respectively.[47] Support for the tautomerization steps was the observation that Nb_2O_5 alone catalyses the deuteration of the aromatic C-H groups with solvent D_2O as demonstrated by ^2H NMR and MS experiments (Figure S-5 and Scheme S-1). Notably, even though this reaction was run under H_2, no HDO of p-cresol occurred in the absence of Ru/C. Therefore, all the dehydration reactions should be primarily catalysed by Ru/C. This point was verified by examining the reactions of a mixture of propyl cyclohexanol (**3**) and 2-methoxy-4-propylcyclohexanol with either Ru/C or Nb_2O_5 alone under the standard conditions (SI Table S-3). In the former case, nearly 100% conversion to propyl cyclohexane (**1**) was achieved: however, with Nb_2O_5 alone, conversion was 62% with only 14.5% selectivity towards (**1**) and the remaining products were not identified.

The reactions with deuterated solvents (D_2O, methanol-d_4) and with D_2 summarized in Table 4 provide further insight into the HDO/hydrogenation mechanism(s). Strong isotope effects on the product are observed upon using D_2O and methanol-d_4. These are particularly evident in the Ru/C catalysed HDO steps of (**5**) → (**4**) as well as (**4** & **3**) → (**1** & **2**). What's more, the final pressure in the reactor is lower when using methanol-d_4. An isotope effect was also evident when D_2 (6 bar) replaced H_2 (6 bar) in a reaction with the H_2O/MeOH medium. In this case, the principal isotope effect was some decrease in ring hydrogenation further supporting the view that MeOH and H_2 supply reducing equivalents at distinctly different stages of the reaction.

The stability and reusability tests show this co-catalyst system to be recyclable and stable during the first 32 h in producing a clean cut of C9 hydrocarbons and excellent material balance of isolated products >90%. The catalyst system displayed decreasing activity in the second, third and fourth recycles (Run 3, 4, and 5 in Fig. 6), although propyl cyclohexane was consistently produced in each case. Notably, adding fresh Nb_2O_5 to the system (Run 6, Fig. 6) partially restored the activity

in terms of the production of (**1**), although the product distribution did not match that of a completely fresh catalyst. Thus, a continuous feeding of fresh Nb_2O_5 after the first recycle could improve the total yield of hydrocarbons and maximize the usability of Ru/C catalyst. Ongoing studies will address strategies to minimize catalyst deactivation pathways.

Lastly, subjecting a simulated bio-oil mixture of lignin monomers to the catalyst system optimal for the conversion of DHE, gave a mixture of just the hydrocarbons (**1**) and (**2**). Thus, this system provides the opportunity to funnel complex bio-oil mixtures primarily composed of oxygenated lignins to simple C9 hydrocarbons more compatible with applications as liquid transportation fuels.

Conflicts of interest

The authors have no conflicts to declare.

Acknowledgements

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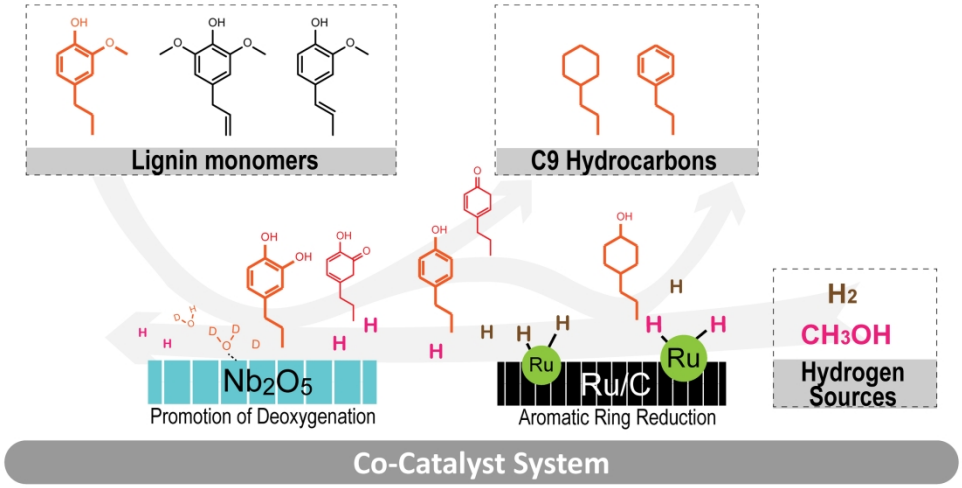

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