Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Journal Name Green Chemistry Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Hydrodeoxygenation of Lignin-Derived Phenols into Alkanes over Carbon Nanotubes Supported Ru Catalysts in Biphasic Systems†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Phenolic compounds derived from lignin are important feedstocks for the sustainable production of alkane fuels with C6-C9 carbons. Hydrodeoxygenation (HDO) is the main chemical process to remove oxygen-containing functionalities. Here, we reported the HDO of phenols in a biphasic H_2O/n-dodecane system. A series of supported Ru catalysts were prepared, characterized and explored for the reaction among which Ru/CNT showed the highest catalytic activity towards the production of alkanes. The model reaction with eugenol achieved a high conversion (>99%) and a high alkane selectivity (98%), which was much higher than the results from the monophasic system (56.5% yield of alkanes in H_2O). The reaction conditions including reaction temperature, hydrogen pressure and the ratio of H_2O/n-$C_{12}H_{26}$ were optimized. The kinetic experiments revealed that eugenol was firstly hydrogenated to 4-propyl-guaiacol, and then deoxygenated into 4-propyl-cyclohexanol which was the main detected intermediate of the reaction. After that, 4-propyl-cyclohexanol was dehydrated and hydrogenated into propylcyclohexane. Moreover, various phenols and dimeric lignin model compounds were also successfully converted into alkanes in the biphasic systems. The construction of biphasic solvent-Ru/CNT catalyst system highlights an efficient route for the conversion of lignin-derived phenolic compounds to biofuels.

1 Introduction

Lignocellulosic biofuels are considered as promising alternatives to the traditional fossil fuels and gaining more and more interests all over the world.[1] Among the main components of lignocelluloses, lignin is a biopolymer consist of phenolic units with a mass fraction of 15-30 wt%, but with a relatively higher energy density than cellulose and hemicellulose.[2] However, due to the complex structure and high oxygen content of lignin, the depolymerized monomers are a mixture of phenols, and difficult to be directly used as chemicals or fuels.[3] To address this problem, hydrodeoxygenation (HDO) was reported as an effective method for the upgrade of this phenolic mixture into conventional transport alkane fuels.[4,5] Previous researches on the HDO of phenols were mainly concentrated on the supported sulfide CoMo and NiMo catalysts which showed good activities towards this conversion.[6] However, these catalysts may cause the sulfur contamination in the product and the fast deactivation of the catalysts.[7] Thus, non-sulfided catalyst systems were required for the HDO of phenolic mixture.[8]

Currently, the reported non-sulfided catalyst systems for the phenols HDO processes can be divided into two types: 1) mixed catalyst systems with a transition-metal based catalyst and a acidic catalyst which are responsible for the hydrogenation and dehydration procedures,[9] respectively (e. g. Pd/C-H_3PO_4[10] and Raney®Ni-Nafion/SiO_2[11]); 2) bifunctional catalysts which combine the active hydrogenating sites and acidic sites into one catalyst. Example of such type catalysts were Ni/HZSM-5,[12] Ru/HZSM-5[13] and others.[14] These systems constitute the significant advances of the HDO of phenols, all of which were conducted in monophasic system such as water or n-decane.[9-15] To our knowledge, the HDO of phenols into alkanes has not yet been performed in a biphasic system, an alternative solvent system to the traditional monophasic media for the production of alkanes form biomass. Thus, we focused on the exploration of HDO of phenols into alkanes in biphasic systems.

Actually, biphasic systems have already been proposed for the conversion of biomass derived compounds into various chemicals and showed remarkable advantages over monophasic systems.[16] For example, recent work from Resasco[17] and Dumesic[18] research groups indicated that biphasic reaction systems showed significant advantages in protecting the products from further degradation by extracting the products produced from the monophasic solvent, simplifying the separation steps to achieve the final products, minimizing the side reactions and increasing the overall yield. Moreover, many biomass-refining processes such as the refining of bio-oil are actually biphasic systems which contains up to 30-40% water.[17a] Compared to separating out the by-products which are hydrophilic through multiple steps, it would be better to carry out sequential reactions in a biphasic system which avoided complicated purification.

Herein, we report the HDO of phenols into cycloalkanes in biphasic system water/n-dodecane over heterogeneous Ru catalysts supported on carbon nanotubes (CNT), a new material with high surface area, high mechanical strength and good chemical stability.[19] The catalyst was well characterized and tested in the HDO of eugenol. Different reaction conditions were evaluated to obtain the highest product yield. The catalyst was also applied to the HDO of other phenols and dimeric lignin model compounds to yield alkanes. Kinetic study was also carried out to gain preliminarily insight into the reaction mechanism.

2 Experimental

Materials

Multi-walled carbon nanotubes (MWCNTs, diam: 10–20 nm, length: 5-15 μm), 5 wt% Pt/C, AC, eugenol, Di-p-tolyl ether, tert-butylcyclohexane and benzyl phenyl ether were supplied by TCI. 5 wt% Pd/C was supplied by Sigma Aldrich. 5 wt% Rh/C, 5 wt% Ru/C, $RuCl_3 \cdot 3H_2O$ (Ru: 37 wt %), ZrO_2, CeO_2, 4-propylphenol and n-dodecane were supplied by Aladdin Industrial Inc. 4-n-propylguaiacol was prepared according to the previous reported method.[3a]

Catalyst characterization

Micromeritics ASAP 2020 analyzer (Tristar II 3020M) was used to measure nitrogen adsorption/desorption and CO adsorption isotherms. The surface area was determined through the Barrett-Emmet-Taller (BET) method. The BarretJoyner-Halenda method was used to determine the the average pore size and pore volume. X-ray power diffraction (XRD) patterns of Ru/CNT, Ru/C, Ru/ZrO_2 and Ru/CeO_2 were measured on an X'pert (PANalytical) diffractometer at 40 kV and 40 mA.

Transmission electron microscopy (TEM) microphotographs were acquired on a JEOL-2010 electron microscope. The samples were suspended in methanol. Scanning electron microscopy (SEM) microphotographs were performed using a SIRION 200 electron microscope. Scanning transmission electron microscopy (STEM) microphotographs and element mapping were performed on a JEM-2100F electron microscope. A Thermo Scientific Escalab 250-X-ray photoelectron spectrometer was used for X-ray photoelectron spectra (XPS) analysis of supported-Ru catalysts.

Catalysts preparation

All of the supported Ru catalysts in this study were prepared by the wetness impregnation methods. For 5 wt% Ru/CNT, Ruthenium(III) trichloride ($RuCl_3 \cdot 3H_2O$, 0.1422g) was dissolved in 10ml water, then the aqueous solution was added to the solution (30 ml H_2O) containing 1.0 g CNT. The mixture was stirred at room temperature for 12 h. After impregnation, the mixture was transferred to an oven and dry at 120 ^oC for 12 h to afford the catalyst precursor. The reduction conditions for the precursor were as follows: the temperature raised from room temperature to 250 ^oC at the rate of 5 ^oC/min and kept at 250 ^oC for 4 h; the reduction gas stream was a mixture of H_2 and N_2 (the flow rates were 20 ml/min and 100 ml/min, respectively). After cooling to room temperature, the resulted black powder was collected. The preparation procedures for Ru/AC, Ru/ZrO_2 and Ru/CeO_2 were similar to that of Ru/CNT.

Catalyst test

The HDO reaction was carried out in a 25 ml Parr reactor equipped with a magnetic stirrer. In a typical experiment, eugenol (164 mg, 1.0 mmol), the catalyst and solvents (6 ml n-dodecane and 6 ml water) were added to the reactor. After purging the reactor with hydrogen for 3 times, it was sealed and maintained 5.0 MPa hydrogen pressure at ambient temperature. Reactions were conducted at the corresponding temperatures. After the reaction finished, the reactor was cooled and the organic layer was collected and analyzed by gas chromatograph (GC) and gas chromatograph-mass spectrometer (GC-MS).

3 Results and discussion

Characterization of the catalysts

Figure 1 showed the X-ray powder diffraction (XRD) analysis of the Ru based catalysts with different supports. No obvious diffraction peaks of Ru species were observed. The XRD pattern of Ru/CNT was similar to that from the previously reported work.[20]

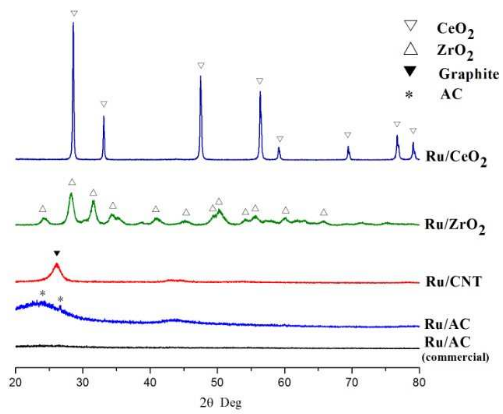


Figure 1. XRD patterns of supported-Ru catalysts

Figure 2 showed the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of Ru/CNT catalysts. The structure and morphology of the catalyst can be clearly seen from the pictures, much of the CNT's structure remained unchanged during the catalyst's preparation procedure. The Ru particles were well distributed on the CNT with a mean size of ~5 nm. Scanning transmission electron microscope (STEM) and the corresponding elemental mapping analysis of the catalyst were also carried out, and the Ru particles can be seen clearly from the STEM images in Figure 3a. The elemental mapping analysis of Ru and C (Figure 3b-3c) of the same section of Ru/CNT gave a direct vision of the distribution of Ru particles.

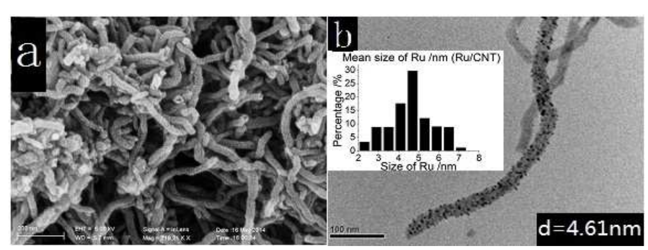


Figure 2. (a) SEM micrograph of 5%Ru/CNT; (b) TEM micrograph of 5%Ru/CNT

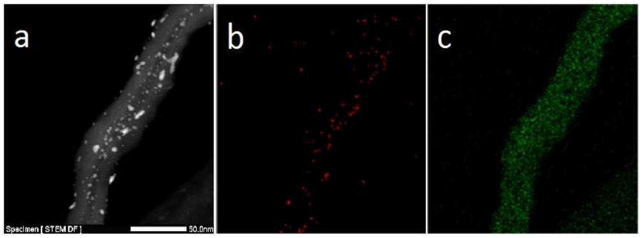


Figure 3. (a) STEM micrograph of 5%Ru/CNT; (b) Elemental mapping of Ru; (c) Elemental mapping of C

X-ray photoelectron spectroscopy (XPS) characterization of Ru metals in the Ru/CNT catalyst was shown in figure 4. The Ru 3p pattern can be divided into three peaks which attributed to the different oxidative state of the Ru species Ru^0 (462.1 eV) and Ru^{4+} (464.2 eV), Ru^{4+} (hydrate) (466.8 eV).[21] The ratio between metallic Ru and oxidative state Ru species (Ru^{4+} and Ru^{4+} (hydrate)) was about 1.01. The high valance Ru species might be further reduced when the catalyst was subjected to the HDO reaction under reductive condition at the specific temperature. The BET analysis of Ru/CNT and other Ru catalysts were also presented in the supporting information. The surface area of Ru/CNT was 201.6 m^2/g with a pore volume and pore size of 0.72 m^3/g and 138.6 Å, respectively. The characterization of the other catalysts were also carried out and presented in the supporting information.

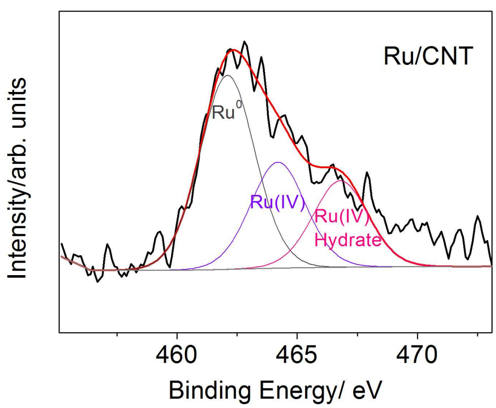


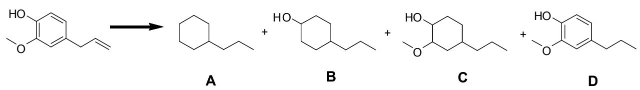
Figure 4. XPS spectra in Ru 3p region for Ru/CNT

Hydrodeoxygenation of eugenol

Initial experiments were carried out to investigate the catalysts' activities towards the HDO of eugenol in monophasic and biphasic system. A variety of carbon-supported noble metal catalysts Ru/C, Pt/C, Pd/C and Rh/C were tested for the catalytic activities and the final products were extracted and analyzed by GC-MS. The products after the reaction were propylcyclohexane (**A**), 4-propyl-clohexanol (**B**), 2-methoxy-4-propyl-cyclohexanol (**C**) and 2-methoxy-4-propylphenol (Table 1, entry 1). However, the selectivity of the target product alkane for Pt/C was only 3.5%, together with a lot of ring hydrogenation products. When biphasic system was used, the products were still a mixture with even lower alkane yield (Table 1, entry 2). For other supported metal catalysts Pd/C and Rh/C, the main products were the ring hydrogenation products C, the oxygen-containing function group were difficult to be cleaved (Table 1, entries 3-6). When Ru/C catalyst was used, the alkane yield increased to 59.5%, the highest yield of the reactions catalyzed by the selected catalysts, which implied that Ru is more active for the cleavage of the C-O bonds (Table 1, entry 7). However, the total products yield extracted from aqueous solution was only about 60%, and the other products cannot be collected and detected, which might be attributed to the decomposition of the formed alkanes under the current reaction conditions. Similar results can also be found in the other reported literatures.[14b, 15a] Noteworthy, when biphasic system $H_2O/n\text{-}C_{12}H_{26}$ was used, the total detected products were sum up to 83% which was higher than that from aqueous system (Table 1, entry 8). The possible reason for this phenomenon was that the products could be quickly moved into organic phase after its production. Meantime, the raw materials would be converted into target products in quantity in aqueous phase, and leading to an obvious increase in alkane yields.

In order to further improve the product yield, we next turned to the Ru based catalysts with different supports which might also be a critical factor in determining the product yield and selectivity. We were excited to find that an almost quantitative yield of alkanes (98%, including 94% propylcyclohexane and 4% propylcyclopentane) was achieved when biphasic solvent system $H_2O/n\text{-}C_{12}H_{26}$ was used in the Ru/CNT catalyzed HDO reaction under the specific reaction conditions. In contrast, the alkane product propylcyclohexane obtained in the monophasic system (H_2O) was only 56.5%. The addition of organic solvent $n\text{-}C_{12}H_{26}$ to the aqueous system increased the collectable alkane products to 98%. When the reaction carried out in pure n-dodecane, the yield of propyocyclohexane was only 4% (Figure 6). When the HDO reaction was carried out in pure n-dodecane, the yield of propylcyclohexane was only 4% and the main product was 4-propyl-cyclohexanol, the main intermediate of the reaction. This result revealed that the aromatic ring could be hydrogenated in the organic solvent over the hydrogenating site but the deoxygenation step (dehydration) was difficult to proceed in the absence of acids. Previous work on the HDO of phenols in water showed that the H_2O could generated the *in situ* H^+ for the dehydration of the oxygenation-containing groups at evaluated temperature.[22] Thus, we reasoned that water was a key factor for the HDO of lignin derived phenols.The above results implied that biphasic system did have the advantages in protecting the products and increasing the products yield over monophasic systems. Also, for comparison, Ru/ZrO_2 and Ru/CeO_2 were prepared and used in the model reaction, but showed poor catalytic activities in catalyzing the eugenol into alkanes. The biphasic systems with these two catalysts still gave higher product yields than aqueous systems which further confirmed that the biphasic systems could protect the organic molecules from decomposition and increased the products yield.

Table 1 Hydrodeoxygenation of eugenol over various catalysts



Entry	Catalyst	Solvent	Conv. /%.	Yield/% A	B	C	D
1	Pt/C	H_2O	100	3.5	18.6	45.7	15.7
2		$H_2O/n\text{-}C_{12}H_{26}$	100	0.2	5.8	17.3	59.2
3	Pd/C	H_2O	100	0.5	5.2	93.9	0.2
4		$H_2O/n\text{-}C_{12}H_{26}$	100	0.1	4.3	95.3	0.1
5	Rh/C	H_2O	100	9.7	7.6	58.4	1.5
6		$H_2O/n\text{-}C_{12}H_{26}$	100	1.9	12.9	78.2	5.9
7	Ru/C	H_2O	100	59.5	3.1	0.3	-
8		$H_2O/n\text{-}C_{12}H_{26}$	100	21.5	26.2	35.2	-
9	Ru/CNT	H_2O	100	56.5	2.1	0.4	-
10		$H_2O/n\text{-}C_{12}H_{26}$	100	94	1.0	-	-
11	Ru/ZrO_2	H_2O	100	29.2	2.4	24.7	0.1
12		$H_2O/n\text{-}C_{12}H_{26}$	100	45.7	5.5	40.0	0.2
13	Ru/CeO_2	H_2O	100	7.4	12.5	47.0	0.2
14		$H_2O/n\text{-}C_{12}H_{26}$	100	12.7	60.5	25.6	0.2

[a] Reaction conditions : eugenol (1 mmol), catalysts (50 mg), n-$C_{12}H_{26}/H_2O$= 6/6 ml , 5 MPa H_2, 220 °C, 3 h.

As reported in the previous literatres,[23] the advantages of CNT supports lie in the following aspects: 1) the mesoporosity of CNT allows significant decreases on mass-transfer limitations; 2) specific metal-support interactions which can directly affect the catalytic activity; 3) specific adsorption properties mainly due to their peculiar morphology, the role of defects and opening/closing of the tubes. Thus, the different catalytic performances between Ru/CNT and other Ru based catalysts in biphasic system may lie in the unique structure of the CNT that led to smaller size of the Ru particles and promoted the contact of the catalysts and substrates. All of the above advantages of Ru/CNT may lead to a superior activity in the HDO reactions in biphasic system.

Effect of different organic solvents

According to the results in Table 1, the organic solvent had a significant impact on the products distribution and selectivity. Therefore, several organic solvents such as methyl isobutyl ketone (MIBK), γ-valerolactone (GVL), cyclohexane (C_6H_{12}), n-octane (n-C_8H_{18}), n-tetradecane (n-$C_{14}H_{30}$) and n-dodecane (n-$C_{12}H_{26}$) were used for the HDO of eugenol under the specific condition. Figure 5 shows the propylcyclohexane yields with different organic solvents. Obviously, the biphasic systems with oxygen-free alkane solvents such as cyclohexane, n-octane, n-tetradecane and n-dodecane led to higher alkane yields over the aqueous system. In contrast, the use of oxygen-containing organic solvents such as methyl isobutyl ketone and γ -valerolactone as the organic phase for the biphasic systems gave lower propylcyclohexane yields. Besides, the oxygen-containing organic solvents were not stable under the HDO reaction condition and reacted together with the eugenol. Thus, long-chain alkanes would be better candidates for the biphasic solvent systems.

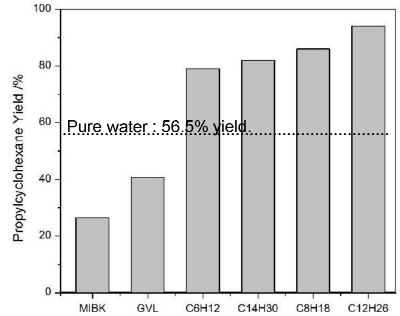


Figure 5. Effect of different organic solvents. Reaction conditions: Eugenol (1 mmol), catalysts (50 mg), Organic solvent/water= 6/6 ml, 5 MPa H_2, 220 °C, 3 h.

Effect of the ratio of organic solvent/water

To better understand the influence of the organic phase on the product distribution, further studies were carried out to investigate the effect of ratio of organic solvent/water. Figure 6 presents the product distribution when using different ratios of organic solvent/water. The reaction carried out in monophasic water gave a 56.5% yield of propylcyclohexane. The addition of about 4% (v/v) organic solvent n-dodecane to water increased the alkane yield to 82%. The reaction reached a maximum alkane yield 94% when the ratio was 1:1. Further increasing the organic solvent ratio led to a decrease of the yield. It is worth noting that the yield of propylcyclohexane was only 4% when the reaction carried out in pure organic phase, and the major products were 2-methoxy-4-propyl-cyclohexanol and 4-propyl-clohexanol, which indicated that water was essential for these reactions to afford alkanes. A possible explanation for the above results was that H^+ ion generated from water through the hydrothermal conditions could act as the acid that help the deoxygenation of the oxygen-containing groups.

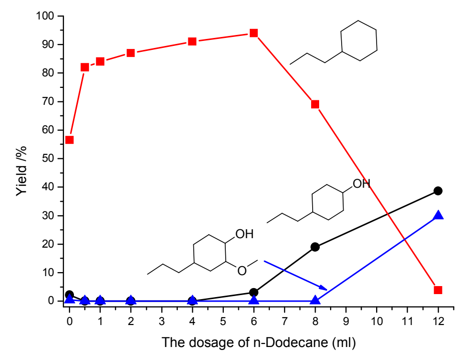


Figure 6. Effect of the Dosage of organic solvent , Total volume of the solvent : 12ml. Reaction conditions : eugenol (1 mmol), catalysts (50 mg), 5 MPa H_2, 220 °C, 3 h.

Effect of the reaction temperature and hydrogen pressure

Figure 7 shows the HDO results under different reaction temperature. When the reaction was carried out under lower reaction temperature (160-200 °C), 4-propyl-clohexanol was the main product (91%) and only a small amount of alkane was formed. Then, increasing the reaction temperature led to a sharp increase of the alkane yield, and 4-propyl-clohexanol decreased to a negligible level, which indicated that 4-propyl-clohexanol might be the intermediate of the reaction. Increasing the reaction temperature was favorable for the deoxygenation step to remove the oxygen-containing groups. The model reaction reached a maximum yield of 94% at 220 °C. Further increasing the temperature led to a decrease of the propylcyclohexane yield which may attribute to the decomposition of the alkanes to small molecules that cannot be detected. The experiments on reaction temperature revealed that desired reaction temperature could effectively accelerate the HDO process and minimize the decomposition of the alkane to afford the highest yield of propylcyclohexane.

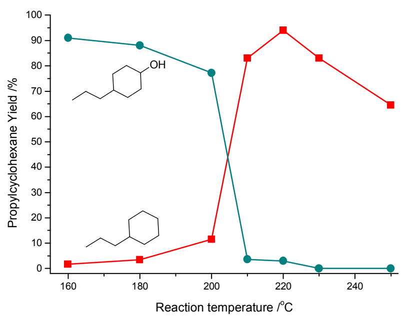


Figure 7. Effect of reaction temperature. Reaction conditions: eugenol (1 mmol), catalysts (50 mg), n-$C_{12}H_{26}/H_2O$ = 6/6 ml, 5 MPa H_2, 3 h.

Effect of the reaction pressure

In addition to the reaction temperature, the reaction pressure was another important parameter to establish a proper condition for the efficient conversion of eugenol. Figure 8 shows the reaction products distribution under different reaction pressure. The conversions of eugenol were >99% under all the investigated pressure from 1.0 MPa to 6.0 MPa. The reaction conducted under 1MPa H_2 afforded 2-methoxy-4-propyl-phenol (22.6%), 2-methoxy-4-propyl-cyclohexanol (12.7%) and 4-propyl-clohexanol (42.4%), the yield of propylcyclohexane was just 5.4%. Further increasing the reaction pressure from 2.0 MPa to 5.0 MPa led to an increase of the propylcyclohexane yield (from 31.4% to 94%). However, higher pressure (6.0 MPa) would lead to the cleavage of C-C bonds of propylcyclohexane and result in a decreased propylcyclohexane yield (90%).

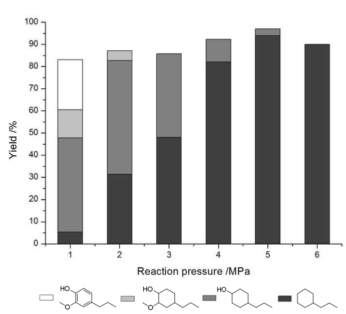


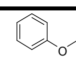
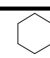
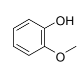
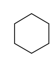
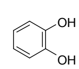
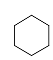
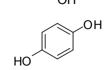
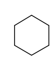
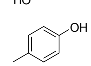
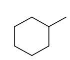
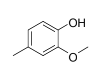
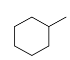
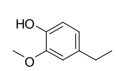
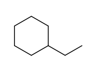
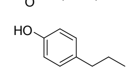
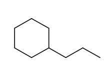
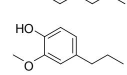
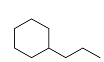
Figure 8. Effect of the reaction pressure. Reaction conditions: eugenol (1 mmol), catalysts (50 mg), n-$C_{12}H_{26}/H_2O$ = 6/6 ml, 220 °C, 3 h.

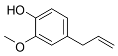
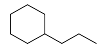
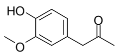
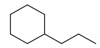
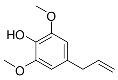
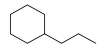
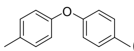
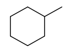
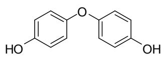
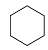
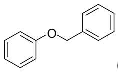
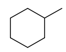
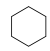
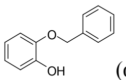
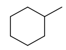
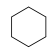
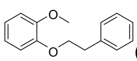
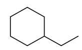
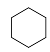
Hydrodeoxygenation of other phenolic compounds

To investigate the scope of the current catalytic system in the biphasic system, a series of lignin-derived phenolic compounds (including monomers and dimers) were evaluated under the optimized conditions (Table 2). Hydrodeoxygenation of lignin-derived phenolic monomers containing six to nine carbon atoms such as anisole, guaiacol, catechol, 4-methylphenol, 4-ethylguaiacol and 4-propylphenol gave moderate to good yields of alkanes (Table 2, entries 1-12). Under the optimized condition, high selectivities (>90%) towards alkanes were achieved for most of cases explored, at the full conversion of phenols. For phenols with lower reactivities, the alkane selectivities were lower (Table 2, entries 6, 7 and 12). We further investigated the HDO of more complicated dimeric lignin model compounds. According to the reported work from Lercher, Zhao et al. that β-O-4, α-O-4, and 4-O-5 linkages were the most common types of C-O bonds in hardwood lignin.[24] All of these three linkages could be converted to the corresponding alkanes effectively, as shown in Table 2, entries 13-17.

Besides, the phenols separated from crude bio-oil were also investigated in the biphasic systems (see SI). The crude bio-oil was obtained by flash pyrolysis of rice husk at 550-600 °C according to the previous work and phenols were separated from the crude bio-oil by a modified glycerol-assisted distillation technology[25]. The separated phenols were treated by NaHCO3 solution, extracted by hexane and evaporated. The mixture of phenols were then submitted for the HDO procedure in biphasic systems. About 25 wt% alkanes were obtained after the HDO reaction. The GC-MS analysis of the extracted phenols and alkanes were also presented in the supporting materials. The application of the biphasic system to these phenols further demonstrated that biphasic system with Ru/CNT catalyst showed great potential of being applied for the upgrade of bio-oil.

Table 2. Hydrodeoxygenation of other lignin-derived phenolic compounds over Ru/CNT in biphasic system

Entry[a]	Substrates		GC yield (%)
1			91
2			92
3			91
4			90
5			92
6			85
7			86
8			96
9			94

10			94		
11			90		
12			80		
13	 (4-O-5)		89		
14	 (4-O-5)		64		
15	 (α-O-4)		44		95
16	 (α-O-4)		61		90
17	 (β-O-4)		53		48

Reaction conditions: Substance (1 mmol), catalysts (50 mg), n-$C_{12}H_{26}/H_2O$ = 6 / 6 ml, 5.0 MPa H_2, 220 ºC, 3 h

Recyclability of the catalyst

The recyclability of the catalyst was an important parameter of the heterogeneous catalyst. Thus, the Ru/CNT catalyst was collected after the reaction and washed by dodecane, after that, the catalyst was directly used for the next run. The product yields were listed in figure 9. The catalyst was used for five times and maintain a good activity, with only a slight decrease in the product yield. The XPS analysis of the used catalysts showed that Ru (IV) and Ru (IV)(hydrate) particles were further reduced into Ru^0 particles under the reductive reaction condition..

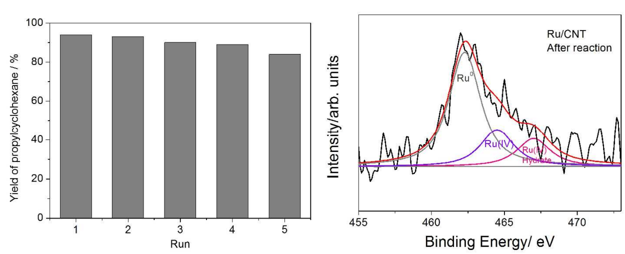


Figure 9. Recycle of the catalyst and the XPS analysis of the used catalyst. Reaction conditions: eugenol (1 mmol), catalysts (50 mg), n-$C_{12}H_{26}/H_2O$ = 6/6 ml, 5.0 MPa H_2, 220 °C, 3 h.

Mechanism

In order to gain preliminary insight into the reaction mechanism, the reaction was traced and analyzed at different reaction time (Figure 10). The intermediates 4-propylcyclohexanol and 2-methoxy-4-propyl-cyclohexanol were formed as the reaction started at the first 10 min, the propylcyclohexane yield was only 3.1%. Then, 2-methoxy-4-propyl-cyclohexanol decreased gradually while 4-propylcyclohexanol increased with a maximum yield of 74.3% at 30 min which was decreased until the end of the reaction. The alkane product propylcyclohexane increased along with the reaction time and reached the highest yield at 180 min. According to the above result, a possible reaction mechanism was proposed, similar to the work reported in the previous work (Figure 11).[8f, 10a, 15a] Eugenol was firstly hydrogenated to 2-methoxy-4-propyl-phenol, and then hydrogenated to 2-methoxy-4-propyl-cyclohexanol. The methoxy functional group was then cleaved to 4-propyl-cyclohexanol. It was then dehydrated and hydrogenated into propylcyclohexane.

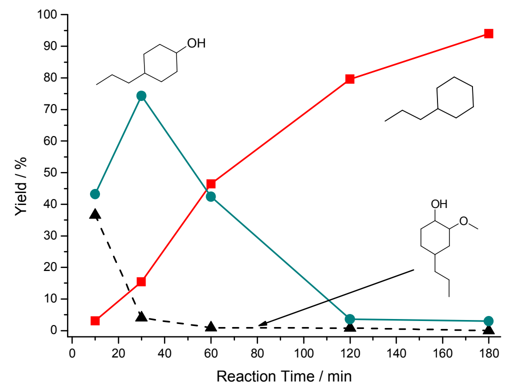


Figure 10. Effect of reaction time. Reaction conditions: eugenol (1 mmol), catalysts (50 mg), n-$C_{12}H_{26}/H_2O$ = 6/6 ml, 5 MPa H_2, 220 °C.

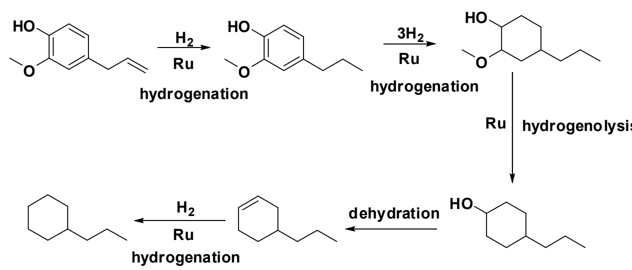


Figure 11. Proposed reaction pathway.

Conclusions

In conclusion, the hydrodeoxygenation of lignin-derived phenolic monomers and dimmers into alkane fuels has been performed with Ru/CNT in n-dodecane/water biphasic system. Under optimized conditions, >99% conversion of eugenol with a high alkanes selectivity (98%, including 94% propylcyclohexane and 4% propylcyclopentane) was achieved. Biphasic systems showed superior advantages over monophasic systems in the HDO reactions. Besides, the unique structure of CNT helped improving the selectivity towards propylcyclohexane. The kinetic experiments revealed that eugenol was converted into propylcyclohexane through the reaction intermediates 2-methoxy-4-propyl-cyclohexanol and 4-propyl-cyclohexanol. The current research emphasized an efficient biphasic catalyst system for transforming lignin-derived phenolic compounds into alkane fuels.

Acknowledgements

This work was supported by the 973 Program (2012CB215306), NSFC (21325208, 21172209, 21272050), CAS (KJCX2-EW-J02), SRFDP (20123402130008), FRFCU and PCSIRT.

Notes and references

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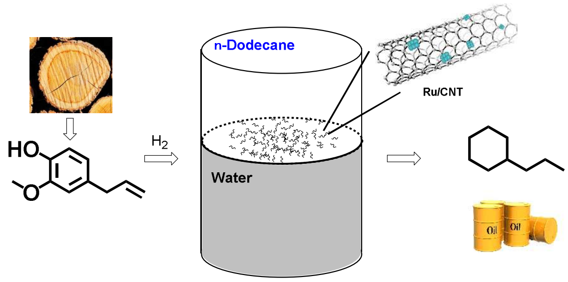

Lignin derived phenols and dimers were converted into alkanes through HDO process over Ru/CNT catalysts in biphasic solvents.