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Title	Hydrodeoxygenation of phenols as lignin models under acid-free conditions with carbon-supported platinum catalysts
Author(s)	Ohta, Hidetoshi; Kobayashi, Hirokazu; Hara, Kenji et al.
Citation	Chemical Communications, 47(44), 12209-12211 https://doi.org/10.1039/c1cc14859a
Issue Date	2011-11-28
Doc URL	https://hdl.handle.net/2115/50126
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Type	journal article
File Information	CC47-44_12209-12211.pdf



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Hydrodeoxygenation of phenols as lignin models under acid-free conditions with carbon-supported platinum catalysts

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

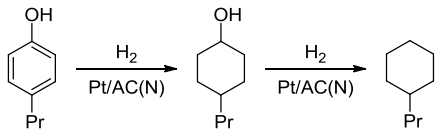
Carbon-supported Pt catalysts are highly active and reusable for the aqueous-phase hydrodeoxygenation of phenols as lignin models without adding any acids. It is suggested that Pt/carbon facilitates the hydrogenation of phenols and the hydrogenolysis of the resulting cyclohexanols.

Bio-oils derived from lignocellulosic biomass have attracted significant attention as a feedstock for the renewable production of biofuels that are an promising alternative to fossil fuels.[1] Lignin is the second most abundant natural organic polymer consisting of methoxylated phenylpropane units, which is a rich source of phenolic bio-oils.[2,3] However, the bio-oils are highly oxygenated, thus leading to undesirable properties and chemical instability. Therefore, the upgrading is necessary for the utilization of bio-oils.[1,3] Hydrodeoxygenation with supported CoMo and NiMo sulfides is the most common process for the upgrading of such bio-oils into transportation fuels.[4] However, these systems suffer from coke formation, sulfur contamination, and water-induced catalyst deactivation.[5] For that reason, non-sulfided catalyst systems have been developed for the hydrodeoxygenation of phenolic bio-oils.[6]

Recently, Kou and Lercher et al. reported the aqueous-phase hydrodeoxygenation of phenolic bio-oils into cycloalkanes by using Pd/C with a liquid acid catalyst (H_3PO_4).[7] The reaction consists of metal-catalyzed hydrogenation of aromatic ring/cycloalkene and acid-catalyzed dehydration of cycloalkanol to cycloalkene. However, the addition of acid catalyst is necessary and the recovering of the acid from the reaction mixture is difficult. The combination of RANEY Ni and a solid acid (Nafion/SiO_2) has also been reported,[8] but the thermal stability of Nafion is not sufficient under at high temperature (typically 300 °C). Accordingly, the development of new heterogeneous catalysts with high activity and durability is still important for the hydrodeoxygenation reaction.

In the present study, we found that readily available carbon-supported Pt catalysts showed high activity and durability in the hydrodeoxygenation of phenols without adding any acid catalysts (Scheme 1). Here, the deoxygenation of phenols includes the hydrogenation of aromatic rings and the subsequent hydrogenolysis of the C-O bond of cyclohexanols.

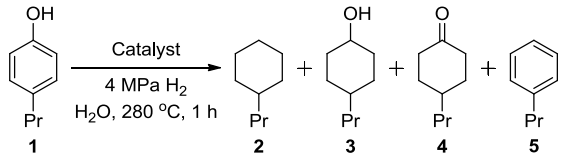
A series of carbon-supported Pt catalysts (2 wt% Pt loading) were prepared by a typical impregnation method using an aqueous solution of H_2PtCl_6 with different types of carbon materials such as AC(N) and AC(W) (activated carbons from Norit and Wako), CMK-3 (mesoporous carbon),[9] MWCNT (multi-walled carbon nanotube, TCI), and BP2000 (carbon black, Cabot). The catalysts were characterized by N_2 adsorption, XRD, and TEM analyses. The characterization data are summarized in Table S1 and Fig. S1-2 in ESI†.



Scheme 1 Reaction pathway for the hydrodeoxygenation of phenols.

The catalytic performances of the carbon-supported Pt catalysts were examined in the hydrodeoxygenation of 4-propylphenol (**1**) in water at 280 °C under 4 MPa H_2 (initial pressure at RT) (Table 1). Pt/AC(N) catalyst, which was prepared from easily available AC(N) support, showed remarkably high catalytic activity to give propylcyclohexane (**2**) in 97% yield (entry 1, Fig. S3 in ESI†). Pt/CMK-3 and Pt/MWCNT also afforded **2** in slightly lower yields (entries 2–3). Pt/AC(W) gave **2** in 73% yield and 4-propylcyclohexanol (**3**) in 16% yield (entry 4), suggesting the reaction pathway as shown in Scheme 1. By contrast, Pt/BP2000 provided markedly lower conversion of **1** (16%) and yield of **2** (9%) (entry 5). Oxide-supported Pt/ZrO_2, Pt/TiO_2, and Pt/CeO_2 were moderately effective for this reaction, affording **2** in good yields (entries 6–8). In these cases, propylbenzene (**5**) was also obtained in 3–10% yield probably via the direct hydrogenolysis of **1**. In sharp contrast, Pt/γ-Al_2O_3 gave no reaction due to the structural transformation of γ-Al_2O_3 into boehmite [AlO(OH)] during the reaction (entry 9, Fig. S4 in ESI†). Besides, Rh, Ru, and Pd catalysts supported on AC(N) were also used (entries 10–12), but these catalysts gave lower yields of **2** than Pt/AC(N) catalyst.[10] With the highly active Pt/AC(N) catalyst, a reaction of **1** on a gram-scale was carried out with a high substrate to catalyst molar ratio (S/C) of 1000 at 280 °C for 2 h, which afforded **2** in >99% yield (entry 13). In the large-scale reaction, an excellent yield (>99%) of **2** was also obtained even at 240 °C with a longer reaction time of 10 h (entry 14). Furthermore, Pt/AC(N) also catalyzed the conversion of **1** into **2** without water-solvent (entry 15), which shows that the catalyst is applicable both in water and under the solvent-free conditions.

Table 1 Hydrodeoxygenation of 4-propylphenol (**1**) with supported metal catalysts.[a]



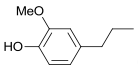
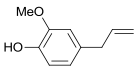
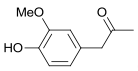
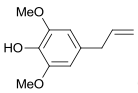
1 **2** **3** **4** **5**

Entry	Catalyst	Conversion (%)	Yield (%)			
			2	**3**	**4**	**5**
1	Pt/AC(N)[b]	100	97	<1	0	0
2	Pt/CMK-3	100	92	0	0	0
3	Pt/MWCNT[c]	100	92	1	<1	0
4	Pt/AC(W)[d]	100	73	16	<1	0
5	Pt/BP2000[e]	16	9	1	0	1
6	Pt/ZrO_2[f]	100	66	<1	0	10
7	Pt/TiO_2[g]	100	77	2	0	3
8	Pt/CeO_2[h]	100	83	<1	0	8
9	Pt/γ-Al_2O_3[i]	0	0	0	0	0
10	Rh/ AC(N)[b]	100	83	<1	0	0
11	Ru/ AC(N)[b]	100	55	<1	0	0
12	Pd/ AC(N)[b]	84	22	57	2	<1
13[j,k]	Pd/ AC(N)[b]	100	>99	0	0	0
14[j,l]	Pd/ AC(N)[b]	100	>99	0	0	0
15[j,m]	Pd/ AC(N)[b]	100	>99	0	0	0

[a] Reaction conditions: 4-propylphenol **1** (2.0 mmol, 272 mg), catalyst (2 wt% metal, S/C = 200), water (40 ml), initial H_2 pressure at RT = 4 MPa, 280 °C, 1 h, stirred at 600 rpm. [b] Activated carbon, SX Ultra (Norit). [c] Multi-walled carbon nanotube (TCI). [d] Activated carbon (Wako). [e] Carbon black Black Pearls 2000 (Cabot). [f] JRC-ZRO-2. [g] P-25, Deggusa. [h] JRC-CEO-2. [i] JRC-ALO-2. [j] 10 mmol (1.36 g) of **1** was used (S/C = 1000). [k] 280 °C, 2 h. [l] 240 °C, 10 h. [m] Without water, 280 °C, 4 h.

The hydrodeoxygenation of guaiacols and syringols was also studied with Pt/AC(N) catalyst in water solvent (Table 2). Under the conditions (4 MPa H_2, 280 °C, 6 h), 4-propylguaiacol (**6**), 4-allylguaiacol (**7**), and 4-acetonylguaiacol (**8**) were efficiently converted to propylcyclohexane **2** in 65–78% yields (entries 16–18, Fig. S5). A derivative of syringol, 4-allyl-2,6-dimethoxyphenol (**9**), also afforded **2** in 58% yield (entry 19). In these reactions, the methoxy group was hydrolyzed to give methanol in 2–3% yields.[7,8] The low yields of methanol might be due to its evaporation or decomposition. In addition, propylcyclopentane (**10**) with a shorter carbon-chain (C8) was obtained in 5–10% yields possibly via skeletal isomerization and hydrogenolysis of cycloalkane.[7,8] Without the solvent, the reaction of **6** gave the hydrodeoxygenation products **2** and **10** in good yields at 300 °C (entry 20).[11] The formation of small amounts of **1** and **5** from **6** suggests the aromatic C−O bond cleavages under the solvent-free conditions.[12] These results indicate that this catalyst system is applicable to the upgrading of various phenolic bio-oils into cycloalkanes.

Table 2 Hydrodeoxygenation of bio-derived phenolic oils with Pt/AC(N) catalyst.[a]

Entry	Substrate	Conversion (%)	Yield (%)[b]		
			 **2**	 **10**	MeOH
16	 **6**	100	78	5	2
17	 **7**	100	66	5	2
18	 **8**	100	65	6	2
19	 **9**	100	58	10	3
20[c]	**6**	97	67	12	2

[a] Reaction conditions: substrate (2.0 mmol), 2 wt% Pt/AC(N) (98 mg, S/C = 200), water (40 mL), initial H_2 pressure at RT = 4 MPa, 280 °C, 6 h, stirred at 600 rpm. [b] Yield based on carbon. [c] **6** (10 mmol, 1.66 g), 2 wt% Pt/AC(N) (488 mg, S/C = 200), without water, 300 °C, 24 h.

The reusability of Pt/AC(N) catalyst was tested for the aqueous-phase reaction of 4-propylphenol (**1**) at 280 °C with the S/C ratio of 1000. After the first reaction (Table 1, entry 13), Pt/AC(N) was recovered by centrifugation, which was successively subjected to the reuse experiments to give **2** in >99% yields (Fig. 1a and Table S2 in ESI†). The pH of the aqueous solution after the first reaction was neutral (pH = 7.0), showing no leaching of acid components from the Pt/AC(N) catalyst. The experiments under the solvent-free conditions also demonstrated the reusability of Pt/AC(N) catalyst (Fig. 1b and Table S2 in ESI†). The XRD patterns of the recovered Pt catalysts showed that the Pt nanoparticles still retained their small sizes (< 2 nm) (Fig. S6 in ESI†), thus indicating that the catalysts were durable under the catalytic conditions.

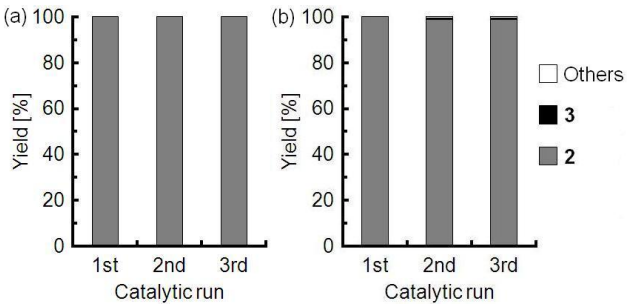


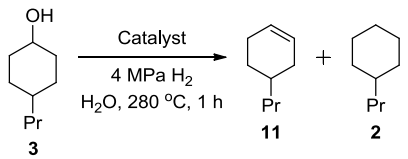
Fig. 1 Reuse experiments in the hydrodeoxygenation of 4-propylphenol (**1**) to propylcyclohexane (**2**) by Pt/AC(N) in water (a) and under solvent-free conditions (b). Reaction conditions: see, entries 13 and 15 in Table 1.

To elucidate the reaction pathway from **1** to **2**, the hydrodeoxygenation of intermediate **3** was also investigated (Table 3).[13] Without catalyst, **3** was dehydrated to form 4-propylcyclohexene (**11**) in 11% yield (entry 21), suggesting that the dehydration was catalyzed by in-situ generated protons (pK_w = 11.2 at 280 °C).[14–16] Accordingly, the addition

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of a base into the reaction completely suppressed the formation of **11** (entry 22). The Pt/carbon catalysts in Table 3 greatly promoted the conversion of **3** to **2**, and among the tested catalysts, Pt/AC(N) afforded the highest yield of **2** (entry 23, 95%). Even in the presence of base, the reaction by Pt/AC(N) gave **2** in good yield (entry 28). The promotional effect is probably due to the enhancement of C-O bond hydrogenolysis by Pt/carbon.[17]

Table 3 Hydrodeoxygenation of 4-propylcyclohexanol (**3**) in water.[a]



Entry	Catalyst	Conversion (%)	Yield (%)	
			11	**2**
21	No catalyst	15	11	0
22	No catalyst[b]	2	0	0
23	Pt/AC(N)	100	0	95
24	Pt/CMK-3	99	0	82
25	Pt/MWCNT	97	0	87
26	Pt/AC(W)	64	0	55
27	Pt/BP2000	100	0	84
28	Pt/AC(N)[b]	66	0	58

[a] Reaction conditions: 4-propylcyclohexanol (2.0 mmol), Pt catalyst (2 wt% Pt, 98 mg, S/C = 200), water (40 ml), initial H_2 pressure at RT = 4 MPa, 280 °C, 1 h, stirred at 600 rpm. [b] $CaCO_3$ (4.0 mmol), pH = 10.

In summary, we have developed a highly efficient carbon-supported Pt catalyst for the hydrodeoxygenation of phenols under acid-free conditions. The Pt/AC(N) catalyst is prepared from readily available AC(N) support and is reusable without loss of catalytic activity. The detailed mechanism and the practical application to lignin are now under study.

This work was financially supported by JSPS KAKENHI (20226016).

Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed preparation, catalytic reaction, characterization methods including XRD patterns, TEM images and N_2 adsorption results in this work. See DOI: 10.1039/b000000x/

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10 In the case of Rh/AC(N) (Table 1, entry 10), propylcyclopentane (<1%) was formed, but no other products were observed on GC of the liquid and gas phases. In the reaction of Ru/AC(N) (entry 11), propylcyclopentane (11%), 2-methylpropylcyclopentane (8%), and some unidentified products were detected in the liquid phase, where the total carbon yield in the liquid phase was 86%. Methane (3%) was observed in the gas phase.

11 In this reaction, **1** (1%), **3** (<1%), **5** (<1%), 2-methoxy-4-propylcyclohexanol (<1%), 2-methylpropylcyclo-pentane (1%), methane (3%), and minor unidentified products were observed.

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13 When the reaction of **3** was performed with Pt/AC(N) under 1 atm of He atmosphere, the dehydrogenation of **3** gave a mixture of 4-propylphenol **1** (15%) and 4-propylcyclohexanone **4** (10%) together with propylcyclohexane **2** (2%), **3** (57%), and propylbenzene **5** (1%). Thus, the reaction of **3** was carried out under pressurized H_2 to evaluate the hydrogenolysis ability of the Pt/carbon catalysts.

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17 NH_3-TPD profiles of Pt/AC(N) and AC(N) showed no peak, suggesting that Pt/AC(N) and AC(N) had no acidity (Fig. S7 in ESI†). Therefore, acid-catalysis of Pt/AC(N) in the reaction of **3** can be excluded.