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## COMMUNICATION

# Low temperature hydrodeoxygenation of phenols under ambient hydrogen pressure to form cyclohexanes catalysed by Pt nanoparticles supported on H-ZSM-5

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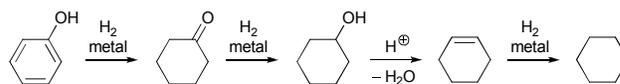
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**The hydrodeoxygenation of various phenols to form cyclohexanes was achieved at 110 °C under an H<sub>2</sub> atmosphere at ambient pressure using a Pt/H-ZSM-5 catalyst and octane as the solvent.**

Interest in the development of a mild and efficient process for converting lignin into fuels or other chemicals has been growing because this would be an effective use of lignocellulosic biomass.<sup>1</sup> Lignin is an abundant and renewable biopolymer that is formed by the polymerisation of phenolic monomers in plants. The hydrodeoxygenation of lignin and lignin-related phenols to produce cyclohexanes (which are used as fuels, solvents and precursors in the synthesis of other useful chemicals) has been the subject of investigations for a long time.<sup>1,2</sup> Many catalyst systems have been developed for the reactions of some lignin-related phenols. However, most of these reactions have been conducted under harsh conditions, with high temperatures (higher than 300 °C) and high H<sub>2</sub> pressures (2–10 MPa), and the catalyst often becomes deactivated mainly because of coking and water-induced structural changes in the catalyst at high temperatures.<sup>3</sup> Furthermore, harsh reaction conditions are undesirable in terms of facility costs and safety. The development of a novel system for catalysing the hydrodeoxygenation of phenols under milder conditions is therefore desirable.

Lercher<sup>4</sup> and Jones<sup>5</sup> showed that the hydrodeoxygenation of phenols to form cyclohexanes can be performed at relatively low temperatures using a metal–acid bifunctional catalyst. For example, the reactions of various phenols proceed at 200–250 °C in the presence of the catalysts Pd/C and H<sub>3</sub>PO<sub>4</sub> in water<sup>4a,4c</sup> via the metal-catalysed hydrogenation of the aromatic ring or a double bond and the acid-catalysed dehydration of the cyclohexanol intermediate (Scheme 1). Similarly, Chen reported that Ru/H-ZSM-5 catalysed the hydrodeoxygenation of phenols in water at 150–200 °C.<sup>6</sup> Kou and Dyson developed an efficient catalyst system composed of nanoparticles of a noble metal and acid-functionalised imidazolium salts, and this catalyst promoted the hydrodeoxygenation of phenol and 4-alkylphenols in ionic liquids at 130 °C.<sup>7</sup> These catalyst systems

were successful in allowing lower reaction temperatures to be used, but high H<sub>2</sub> pressures (4–5 MPa) were still required. Here we report that Pt/H-ZSM-5 efficiently catalyses the conversion of various phenols into cyclohexanes under mild conditions (110 °C, under H<sub>2</sub> at 0.1 MPa, using octane as the solvent).



**Scheme 1** General reaction mechanism for the hydrodeoxygenation of phenol catalysed by a metal–acid bifunctional catalyst.

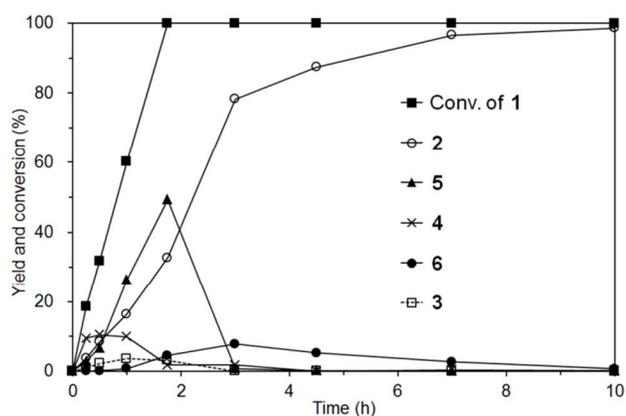
Various zeolite-supported Pt catalysts were prepared. Several kinds of the zeolites (H-ZSM-5, H- $\beta$ , H-MOR and H-Y) were impregnated with an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> to load each zeolite with 2 wt% of Pt, and the zeolites were then dried and reduced in the presence of H<sub>2</sub>. Subsequently, each catalyst was then characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption/desorption measurements and acid–base titration. The characterisation results are summarised in Table S1, Fig. S1 and S2 in the electronic supplementary information.† Of the catalysts that were prepared, Pt/H-ZSM-5 had the smallest Pt particle size (5.6 ± 2.0 nm, by TEM analysis) and the lowest acid content (0.24 mmol g<sup>-1</sup>).

Each Pt catalyst was used to hydrodeoxygenate 4-propylphenol (**1**) in octane at 110 °C for 10 h under H<sub>2</sub> at 0.1 MPa, and the catalytic performances of the different systems were evaluated (Table 1). Pt/H-ZSM-5 was an excellent catalyst, giving propylcyclohexane (**2**) in 99% yield (entry 1). The Pt/H-ZSM-5 catalyst was reused twice without any loss of catalytic activity (entries 2 and 3). A blank test using only H-ZSM-5 as a catalyst afforded no products, showing the importance of Pt nanoparticle as a hydrogenation catalyst (entry 4). Pt/H- $\beta$  and Pt/H-MOR provided **2** in slightly lower yields (entries 5 and 6). In contrast, Pt/H-Y gave **2** in 8% yield and many byproducts including phenol (7%) and 2,4-dipropylphenol (17%), which were probably formed via the acid-catalysed transalkylation<sup>8</sup> of **1** (entry 7). Higher acid contents of Pt/H- $\beta$ , Pt/H-MOR and Pt/H-Y (0.63–1.41

**Table 1** Hydrodeoxygenation of 4-propylphenol (**1**) at 110 °C under H<sub>2</sub> at 0.1 MPa, catalysed by different zeolite-supported metal nanoparticles.<sup>a</sup>

Entry	Catalyst	Solvent	Conv. (%) <sup>b</sup>	Yield based on carbon (%) <sup>b</sup>				
				2	3	4	5	6 <sup>c</sup>
1	Pt/H-ZSM-5	Octane	>99	99	0	<1	0	<1
2	Pt/H-ZSM-5 (2nd use)	Octane	>99	99	0	0	0	<1
3	Pt/H-ZSM-5 (3rd use)	Octane	>99	98	0	<1	0	1
4	H-ZSM-5	Octane	6	0	0	0	0	0
5	Pt/H-β	Octane	>99	92	0	0	0	<1
6	Pt/H-MOR	Octane	>99	89	0	0	0	<1
7	Pt/H-Y	Octane	59	8	3	0	0	<1
8	Rh/H-ZSM-5 + H-ZSM-5 <sup>d</sup>	Octane	>99	88	0	<1	0	2
9	Pd/H-ZSM-5 + H-ZSM-5 <sup>d</sup>	Octane	42	3	<1	18	0	0
10	Ru/H-ZSM-5 + H-ZSM-5 <sup>d</sup>	Octane	8	2	<1	2	0	0
11	Pt/H-ZSM-5	Isoamyl acetate	>99	39	1	0	51	1
12	Pt/H-ZSM-5	Dibutyl ether	>99	32	0	1	37	21
13 <sup>e</sup>	Pt/H-ZSM-5	H <sub>2</sub> O	63	2	3	2	43	0
14 <sup>e</sup>	Pt/H-ZSM-5	1,4-Dioxane	7	2	<1	2	0	0
15	Pt/H-ZSM-5	Butanol	4	<1	2	0	1	0
16	Pt/H-ZSM-5	DMF	<1	0	0	0	0	0
17	Pt/H-ZSM-5	No solvent	12	0	0	3	<1	0

<sup>a</sup> Reaction conditions: **1** (1.0 mmol), 2 wt% Pt/zeolite (98 mg, 1 mol% Pt) or H-ZSM-5 (96 mg), solvent (1.0 mL), 110 °C, H<sub>2</sub> (balloon, 0.1 MPa), 10 h. <sup>b</sup> Determined by gas chromatography. <sup>c</sup> The sum of the yields of all the isomers. <sup>d</sup> 2 wt% metal/H-ZSM-5 (51–53 mg, 1 mol% metal) + additional H-ZSM-5 (the total amount of H-ZSM-5 was 96 mg). <sup>e</sup> At 100 °C.



**Fig. 1** Time course of the hydrodeoxygenation of **1**, catalysed by Pt/H-ZSM-5 in octane. Reaction conditions: **1** (1.0 mmol), 2 wt% Pt/H-ZSM-5 (98 mg, 1 mol% Pt), octane (1.0 mL), 110 °C, H<sub>2</sub> (balloon, 0.1 MPa).

mmol g<sup>-1</sup>) than Pt/H-ZSM-5 may cause undesirable side reactions. Pt/H-ZSM-5 has appropriate amount of acid sites, which would be suitable for efficient and selective hydrodeoxygenation. The catalytic activities of other metal nanoparticles (Rh, Pd and Ru) supported on H-ZSM-5 were examined using the same H-ZSM-5 loadings as were used for Pt/H-ZSM-5. As is shown in entry 8, the yield of **2** was lower when Rh/H-ZSM-5 was used than when Pt/H-ZSM-5 was used. Pd/H-ZSM-5 selectively converted **1** to 4-propylcyclohexanone (**4**)<sup>9</sup> in 18% yield with the formation of **2**, propylbenzene (**3**) and many unidentified byproducts (entry 9). Ru/H-ZSM-5 was not active under the reaction conditions that were used, and it gave only a trace of **2** and a very low conversion rate (entry

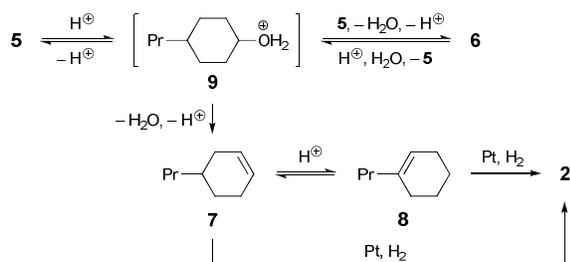
10).<sup>10</sup> It should be noted that the solvent used had a great influence on the catalytic activity of the Pt/H-ZSM-5.<sup>11</sup> The complete conversion of **1** was observed in isoamyl acetate as in octane, but the former case gave **2** in only 39% yield, and 4-propylcyclohexanol (**5**) and bis(4-propylcyclohexyl)ether (**6**) were also obtained in 51% and 1% yields, respectively (entry 11). Similar result was produced with dibutyl ether (entry 12). The formation of **2** was almost completely suppressed when H<sub>2</sub>O, 1,4-dioxane, butanol, DMF and neat conditions were used (entries 13–17). H<sub>2</sub>O is an inevitable byproduct of hydrodeoxygenation, but it will depress the activity of the catalyst compared to octane (entries 1 vs 13). Octane forms an azeotrope with H<sub>2</sub>O and could allow a certain amount of H<sub>2</sub>O to be removed from the reaction system through azeotropic distillation (the azeotropic temperature is 90 °C).<sup>12</sup> In addition, the non-polar octane would have poorly coordinated to the catalyst surface and have little effect on the catalytic activity. The reaction could therefore be accelerated more efficiently by using octane as the solvent.

The time course of the hydrodeoxygenation of **1** catalysed by Pt/H-ZSM-5 in octane is shown in Fig. 1. It can be seen that **1** was gradually hydrogenated as the reaction time increased, and was completely consumed after 1.8 h. After 15 minutes, **4** was formed as a major product in 10% yield. The amount of **4** present then decreased over time, and the amount of **5** produced increased, reaching a yield of 49% after 1.8 h. It can be seen, therefore, that **1** was hydrogenated to **5** via **4**. After 1.8 h, the amounts of **2** and **6** present increased as the amount of **5** present decreased, suggesting that **2** and **6** were formed from **5**. Finally, **6** was completely consumed and converted into **2** after 10 h.

**Table 2** Control experiments using **5** and **6** as substrates.<sup>a</sup>

Entry	Substrate	Catalyst	Gas	Time (h)	Conv. (%) <sup>b</sup>	Yield based on carbon (%) <sup>b</sup>					
						<b>2</b>	<b>4</b>	<b>5</b>	<b>6</b> <sup>c</sup>	<b>7</b> <sup>d</sup>	<b>8</b> <sup>e</sup>
18	<b>5</b>	H-ZSM-5	H <sub>2</sub>	1	34	<1	0	–	0	10	12
19	<b>5</b>	Pt/H-ZSM-5	N <sub>2</sub>	1	39	1	0	–	0	15	13
20	<b>5</b>	Pt/H-ZSM-5	H <sub>2</sub>	1	91	54	4	–	15	0	0
21	<b>5</b>	Pt/H-ZSM-5	H <sub>2</sub>	4	>99	>99	0	–	<1	0	0
22	<b>6</b>	H-ZSM-5	H <sub>2</sub>	6	65	<1	0	<1	–	13	29
23	<b>6</b>	Pt/H-ZSM-5	N <sub>2</sub>	6	56	<1	0	<1	–	11	25
24	<b>6</b>	Pt/H-ZSM-5	H <sub>2</sub>	6	>99	97	0	0	–	0	0

<sup>a</sup> Reaction conditions: **5** (1.0 mmol) or **6** (0.50 mmol), H-ZSM-5 (96 mg) or 2 wt% Pt/H-ZSM-5 (98 mg, 1 mol% Pt for **5**, 2 mol% Pt for **6**), octane (1.0 mL), 110 °C, gas pressure 0.1 MPa supplied using a balloon. <sup>b</sup> Determined by gas chromatography. <sup>c</sup> The sum of the yields of all the isomers. <sup>d</sup> 4-propylcyclohexene. <sup>e</sup> 1-propylcyclohexene.

**Fig. 2** Proposed reaction pathways for the conversion of **5** to **2**.

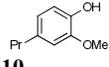
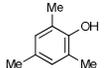
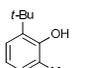
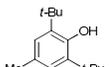
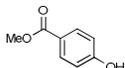
Control experiments using **5** and **6** as substrates were performed to clarify the reaction pathways involved in the conversion of **5** to **2** (Table 2). We consider that **6** is generated through the protonation of **5** to form the corresponding oxonium cation **9** and then the nucleophilic attack on **9** by another molecule of **5**.<sup>13</sup> However, the reactions of **5** with H-ZSM-5 under H<sub>2</sub> (entry 18) and with Pt/H-ZSM-5 under N<sub>2</sub> (entry 19) for 1 h did not give any **6**, and the dominant products were actually 4-propylcyclohexene (**7**) and 1-propylcyclohexene (**8**), formed through the acid-catalysed double-bond isomerisation of **7**.<sup>14</sup> In contrast, the reaction with Pt/H-ZSM-5 under H<sub>2</sub> afforded **2** and **6** after 1 h with higher conversion of **5** (entry 20), suggesting that the formation of **6** was highly dependent on the reaction conditions. With Pt/H-ZSM-5 under H<sub>2</sub>, **5** was fully converted into **2** after 4 h (entry 21). We found that **6** was converted into **7** and **8** by H-ZSM-5 under H<sub>2</sub> (entry 22) and by Pt/H-ZSM-5 under N<sub>2</sub> (entry 23). Under H<sub>2</sub>, the reaction with Pt/H-ZSM-5 resulted in the full conversion of **6** after 6 h, giving **2** in 97% yield (entry 24). From these results, we propose the reaction pathways involved in the conversion of **5** to **2** (Fig. 2). First, **5** is protonated by H-ZSM-5 to give **9**, which is then transformed into **6** through nucleophilic attack by **5** and/or into **7** through dehydration. **6** is gradually converted into **7** via **9** because **6** and **5** are at equilibrium under acidic conditions. The formation of **7** is promoted by the irreversible hydrogenation of **7** and its isomer **8** by Pt/H-ZSM-5 to afford the final product **2**.

We performed the hydrodeoxygenation reaction using various phenols in octane at 110 °C under an H<sub>2</sub> atmosphere (0.1 MPa) at different reaction times to demonstrate the effectiveness of Pt/H-ZSM-5 as a catalyst. Selected results are shown in Table 3. 2-Methoxy-4-propylphenol (**10**), which is one of the most important lignin-related phenols, was converted

into **2** in 67% yield (entry 25).<sup>15</sup> For this reaction, Pt/H-β and Pt/H-MOR showed less catalytic activities, giving **2** in 39% and 40% yields, respectively (the results are not shown in Table 3). The reactions of the sterically demanding compounds 2,4,6-trimethylphenol (**11**) and 2-*tert*-butyl-6-methylphenol (**13**) proceeded smoothly to afford 1,3,5-trimethylcyclohexane (**12**) in 91% yield and 1-*tert*-butyl-3-methylcyclohexane (**14**) in 95% yield, respectively (entries 26 and 27). The strong catalytic activity of Pt/H-ZSM-5 is noteworthy because the hydrogenation of sterically hindered phenols usually requires high pressure H<sub>2</sub>.<sup>16</sup> The expected 1,3-di-*tert*-butyl-5-methylcyclohexane was not obtained when the sterically more encumbered compound 2,6-di-*tert*-butyl-4-methylphenol (**15**) was used, but the de-*tert*-butylated product **14** was formed in 45% yield together with 2,6-di-*tert*-butyl-4-methylcyclohexanone (**16**) in 8% yield (entry 28). A C4 product, derived from the *tert*-butyl group in **15**, should be formed in at least 17% yield; however, we could not detect it probably due to the evaporation or the reaction with other compounds during the reaction (some unidentified byproducts were observed by GC analysis). In this reaction, **14** may have been formed through the acid-catalysed de-*tert*-butylation of **15** followed by the hydrodeoxygenation of the resulting 2-*tert*-butyl-4-methylphenol to give **14**.<sup>17</sup> With Pt/H-β and Pt/H-MOR, **15** was converted to **14** (8% and 8%, respectively) and **16** (<1% and 37%, respectively) together with many unidentified byproducts which were formed probably via the acid-catalysed reactions caused by the zeolites with high acid content (the results are not shown in Table 3). The reaction of methyl 4-hydroxybenzoate (**17**) successfully provided methyl cyclohexanecarboxylate (**18**) in 67% yield without causing the ester moiety to be reduced (entry 29).<sup>18</sup> This kind of transformation would be difficult to achieve using conventional catalyst systems that require harsh reaction conditions.

In summary, we have developed a system for hydrodeoxygenating phenols to form cyclohexanes under mild conditions (ambient H<sub>2</sub> pressure and 110 °C) using Pt/H-ZSM-5 as a catalyst and octane as the solvent. The catalyst system facilitated the reaction of various phenols, including the generally less reactive lignin-related methoxyphenol, sterically hindered alkylphenols and an ester-functionalised phenol. Detailed mechanistic studies and studies of reactions using a broad range of phenols are ongoing, and the results will be reported in due course.

**Table 3** Hydrodeoxygenation of various phenols catalysed by Pt/H-ZSM-5 in octane.<sup>a</sup>

Entry	Substrate	Conv. (%) <sup>b</sup>	Product	Yield (%) <sup>b,c</sup>
25		90		67
26 <sup>d</sup>		>99		91 <sup>e,f</sup>
27		>99		95 <sup>e</sup>
28 <sup>g</sup>		>99		45 <sup>e</sup>
29 <sup>h</sup>		>99		67

<sup>a</sup> Reaction conditions: substrate (1.0 mmol), 2 wt% Pt/H-ZSM-5 (98 mg, 1 mol% Pt), octane (1.0 mL), 110 °C, H<sub>2</sub> (balloon, 0.1 MPa), 24 h. <sup>b</sup> Determined by gas chromatography. <sup>c</sup> Calculated based on carbon. <sup>d</sup> 6 h. <sup>e</sup> The sum of the yields of the isomers. <sup>f</sup> The molar ratio of the *cis,cis*- and *cis,trans*-isomers was 2:3. <sup>g</sup> 2 mol% Pt. <sup>h</sup> 48 h.

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## Notes and references

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- The reaction of **16** was conducted under the same reaction conditions as that of **15**; however, **14** was not obtained at all. Therefore, **16** is not the reaction intermediate for the formation of **14**.
- 2-oxabicyclo[2.2.2]octan-3-one **19** (18% yield) and some unidentified compounds were formed as byproducts. The formation of **19** should be accompanied by methanol formation (3% yield); however, the detection was difficult due to the evaporation. For the formation of **19**, see: T. A. Giudici and T. C. Bruice, *J. Org. Chem.*, 1970, **35**, 2386.

