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Efficient Hydrodeoxygenation of Ketones, Phenols, and Ethers Promoted by Platinum–Heteropolyacid Bifunctional Catalysts

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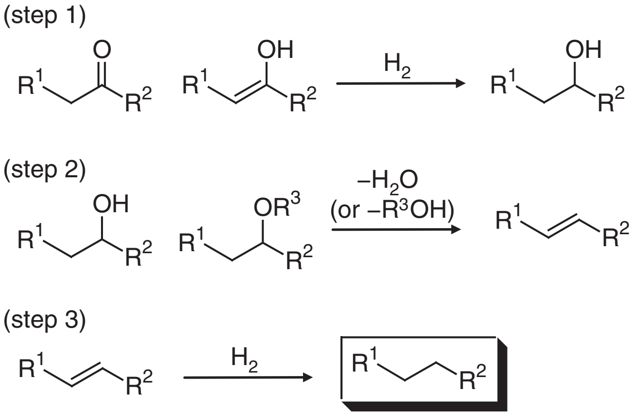
A $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-supported platinum catalyst (Pt/CsPW) could act as an efficient heterogeneous catalyst for hydrodeoxygenation of various types of oxygen-containing compounds such as ketones, phenols, and ethers. The observed catalysis was truly heterogeneous, and the retrieved Pt/CsPW could be reused.

Oxygen-containing compounds such as carbonyls, alcohols, phenols, and ethers are versatile and readily available. They can be employed as precursors for various types of chemicals. Deoxygenation to alkanes (or alkenes) is one of the representative transformations and has frequently been performed in laboratory-scale organic synthesis as well as bulk production.[1] Since oxygen functionalities are poor leaving groups, deoxygenation often requires strong reductants. For example, in laboratory-scale deoxygenation of ketones and aldehydes, Clemmensen reduction using a zinc amalgam under strongly acidic conditions, Wolff–Kishner reduction using hydrazine or its derivatives under strongly basic conditions, and Mozingo reduction through the sequential reaction of thioacetalization and hydrogenolysis are still frequently been utilized despite their production of large amounts of by-products.[2]

In comparison with the above-mentioned antiquated procedures, hydrodeoxygenation (using H_2 as the reductant) is a promising reaction for deoxygenation of oxygen-containing compounds.[3–6] In particular, it has been utilized for upgrading biomass and pyrolysis bio-oils.[3,4] Although several classes of catalysts such as cobalt–molybdenum and nickel–molybdenum have industrially been utilized, they readily undergo deactivation due to coke deposition.[7] In addition, these procedures typically require harsh reaction conditions (e.g., ≥300 °C for phenols).[3a]

The above disadvantages can be overcome by the one-pot strategy using metal–acid bifunctional catalysts.[4–6] As shown in Scheme 1, hydrogenation of carbonyls or phenols to saturated alcohols proceeds (step 1), followed by the formation of alkenes through dehydration of the alcohols (step 2). Finally, the alkenes are hydrogenated to give the corresponding alkanes (step 3). Although several metal–acid bifunctional catalysts have been developed for this strategy, challenges still remain because they have disadvantages of limited substrate scopes, high temperatures, high pressures of H_2, and/or use of large excess of H_2.[4–6]

Herein, we report that hydrodeoxygenation of oxygen-containing compounds efficiently proceeded in the presence of a $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-supported platinum catalyst (Pt/CsPW) under relatively mild reaction conditions (typically 120 °C, 5 atm of H_2). The present system could be applied to a wide variety of oxygen-containing compounds such as aliphatic and aromatic ketones, phenols, and even ethers, affording the corresponding deoxygenated products (mainly alkanes) in moderate to high yields. The observed catalysis was truly heterogeneous, and the catalyst could be reused without a severe loss of high catalytic performance.

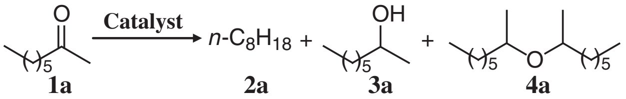


Scheme 1. A possible reaction path for hydrodeoxygenation of oxygen-containing compounds in the presence of metal–acid bifunctional catalysts.

We prepared various metal–acid bifunctional catalysts by impregnation of metals on (acidic) supports using aqueous metal chloride solutions, followed by reduction with H_2 (denoted as metal/support; see the Supporting Information for their preparation).[8] With regard to metals for hydrogenation (steps 1 and 3 in Scheme 1), we used platinum group metals such as platinum, palladium, rhodium, and ruthenium. Alcohol dehydration (step 2 in Scheme 1) is expected to be included in the rate-limiting step for hydrodeoxygenation using metal–acid bifunctional catalysts.[4a,4g,4h] Therefore, we selected heteropolyacids such as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), $Cs_3HSiW_{12}O_{40}$ (CsSiW), $H_3PW_{12}O_{40}$ (HPW), and $H_4SiW_{12}O_{40}$ (HSiW) as acidic supports because of the following reasons: their strong Brønsted acidities for protonation of hydroxy groups[9] and bare nucleophilic surface of polyanions for stabilization of carbocation-type intermediates formed in step 2 in Scheme 1.[10]

By using metal/support catalysts, we initially carried out the hydrodeoxygenation of 2-octanone (**1a**) to octane (**2a**) as the model reaction (Table 1).[11,12] The reaction was carried out at 120 °C (bath temperature) using 0.1 mol % (metal) catalysts under 5 atm of H_2. Under the present conditions, the reaction did not proceed at all in the absence of the catalysts or the presence of CsPW alone (Table 1, Entries 11 and 12). Among various metal/CsPW catalysts examined, Pt/CsPW was the most effective for the hydrodeoxygenation; **1a** was completely converted within 1 h, and **2a**, 2-octanol (**3a**), and dioctyl ether (**4a**) were obtained in 36, 46, and 12% yields, respectively (Table 1, Entry 1). A side reaction of the intermolecular dehydrative condensation of **3a** to **4a** took place in the present

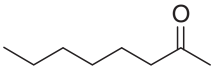
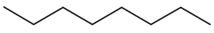
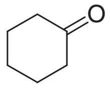
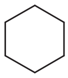
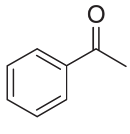
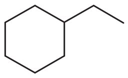
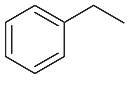
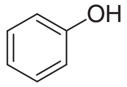
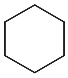
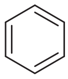
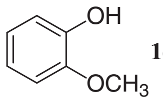
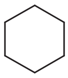
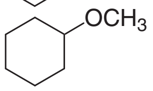
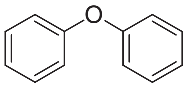
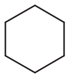
Table 1. Hydrodeoxygenation of **1a** using various catalysts[a]



Entry	Catalyst	Conv. of **1a**/%[b]	Yield/%[b]		
			2a	**3a**	**4a**
1	Pt/CsPW	>99	36	46	12
2[c]	Pt/CsPW	>99	83	3	14
3	Pd/CsPW	38	31	<1	<1
4	Rh/CsPW	12	6	<1	<1
5	Ru/CsPW	18	2	<1	<1
6	Pt/CsSiW	>99	26	64	7
7	Pt/HPW	92[d]	12	59	4
8	Pt/HSiW	>99[e]	11	70	<1
9	Pt/C	66	<1	59	<1
10	Pt/Al_2O_3	40	<1	36	<1
11[f]	CsPW	19	<1	<1	<1
12	None	<1	<1	<1	<1

[a] Reaction conditions: Metal/support (the molar ratio of metal to heteropolyacid: 1/20; metal: 0.1 mol %), **1a** (0.5 mmol), heptane (1 mL), 120 °C, 1 h, H_2 (5 atm). [b] Conversions and yields were determined by GC using naphthalene as an internal standard. Yield/% = (Product/mol)/(**1a**/mol) × 100 (for **2a** and **3a**); Yield/% = (Product × 2/mol)/(**1a**/mol) × 100 (for **4a**). [c] 3 h. [d] Octenes were formed in 14% total yield. [e] Octenes were formed in 5% total yield. [f] CsPW (160 mg).

Table 2. Pt/CsPW-catalyzed hydrodeoxygenation of various kinds of oxygen-containing compounds[a]

Entry	Substrate		Product	Yield /%[b]
1 2[c] 3[c]		**1a**		92 90 76
4		**1b**		92
5[d]		**1c**	 	24 70
6		**1d**	 	92 2
7[e]		**1e**	 	68 2
8[e]		**1f**	 	78 2

[a] Reaction conditions: Pt/CsPW (the molar ratio of Pt to CsPW: 1/100; Pt: 0.1 mol %), substrate (0.5 mmol), heptane (1 mL), 120 °C, 3 h, H_2 (5 atm). [b] Yields were determined by GC using naphthalene as an internal standard. Yield/% = (Product/mol)/(**1**/mol) × 100 (for Entries 1–7); Yield/% = (Product/mol)/(**1f** × 2/mol) × 100 (for Entry 8). [c] Entries 2 and 3 for the 1st and the 2nd reuses, respectively. [d] 60 °C. [e] 9 h, H_2 (7 atm).

system; however, this is not a problem because Pt/CsPW could also catalyze hydrodeoxygenation of ethers to alkanes (see the last section). When prolonging the reaction time to 3 h, the yield of **2a** reached up to 83% (Table 1, Entry 2). Pd/CsPW gave **2a** in a moderate yield (Table 1, Entry 3), while the hydrodeoxygenation hardly proceeded in the presence of Rh/CsPW and Ru/CsPW (Table 1, Entries 4 and 5).

The selection of acidic supports was very crucial. As summarized in Table 1, **2a** was obtained in significant yields only when heteropolyacids were used as supports for platinum. In the case of Pt/C and Pt/Al_2O_3, **1a** was selectively hydrogenated to **3a** without the formation of **2a** (Table 1, Entries 9 and 10), thus indicating that heteropolyacids can efficiently promote the dehydration of **3a**. Indeed, we confirmed in separate experiments that dehydration of alcohols was efficiently promoted in the presence of heteropolyacids. Cesium salts (CsPW and CsSiW) were more effective than the corresponding acid forms (HPW and HSiW) (Table 1, Entries 1 and 6 vs. 7 and 8) possibly owing to the large surface areas of the cesium salts.[13,14] The phosphorous-centered CsPW was a better support than the silicon-centered CsSiW (Table 1, Entries 1 vs. 6).[15]

The comparison of the results (conversions of **1a**) of Pt/CsPW with those of Pt/C and Pt/Al_2O_3 reveals that the hydrogenation of **1a** (ketone) to **3a** (alcohol) was also accelerated by the presence of heteropolyacids. Recently, Kaneda and co-workers have shown that the heterolytic cleavage of H_2 proceeds at the interface between metals and basic oxides (e.g., CeO_2 and hydrotalcite as proton acceptors) and that hydrogenation of polar multiple bonds, e.g., carbonyls, can be promoted by the active hydrogen species.[16] Similarly, in the present case, the heterolytic cleavage of H_2 likely proceeds at the interface between platinum and bare nucleophilic surface of polyanions, resulting in the promotion of ketone hydrogenation (step 1 in Scheme 1).

To verify whether the observed catalysis was derived from solid Pt/CsPW or leached metal species (platinum and/or tungsten), the hydrodeoxygenation of **1a** was performed under the conditions described in Table 1, and Pt/CsPW was removed from the reaction mixture by filtration at ca. 40% yield of **2a**. When the filtrate was again heated at 120 °C (bath temperature) under 5 atm of H_2, no further production of **2a** was observed. In addition, ICP-AES analysis confirmed that no platinum and tungsten species were detected in the filtrate (Pt: <0.06%, W: <0.007%). All these results rule out any contribution to the observed catalysis from metal species that leached into the reaction solution, and the observed catalysis for the present hydrodeoxygenation is truly heterogeneous.[17]

After the hydrodeoxygenation of **1a** was completed, Pt/CsPW could easily be retrieved from the reaction mixture by simple filtration (>89% recovery). We confirmed by IR and

XRD analyses that the local as well as bulk structures of CsPW in the catalyst were preserved after reuse. The retrieved Pt/CsPW could be reused for the hydrodeoxygenation of **1a** at least twice without a severe loss of its catalytic performance (Table 2, Entries 2 and 3).

Finally, we turned our attention to the scope of the present Pt/CsPW-catalyzed hydrodeoxygenation system toward various types of oxygen-containing compounds (Table 2). For hydrodeoxygenation, 1.3–3.8 equiv of H_2 with respect to hydrogenation was utilized. The hydrodeoxygenation of both acyclic (**1a**) and cyclic (**1b**) aliphatic ketones proceeded smoothly to give the corresponding alkanes in high yields (Table 2, Entries 1 and 4). In the case of acetophenone (**1c**), the reaction took place even at 60 °C to form the corresponding deoxygenated products in 94% total yields (Table 2, Entry 5). Beside ketones, lignin-derived phenolic monomers such as phenol (**1d**) and guaiacol (**1e**) also afforded the corresponding alkanes in high yields (Table 2, Entries 6 and 7). Notably, even less reactive diphenyl ether (**1f**) could be converted into cyclohexane in 78% yield (Table 2, Entry 8).

In summary, we successfully developed an efficient heterogeneously catalyzed system for hydrodeoxygenation of various types of oxygen-containing compounds such as ketones, phenols, and ethers. In addition, Pt/CsPW could be reused. In comparison with the previously reported systems, the present system has the following advantages: a wide substrate scope, milder reaction conditions (e.g., temperatures: $\leq$120 °C, H_2 pressures: 5–7 atm), and/or the use of reduced amounts of H_2 (1.3–3.8 equiv with respect to hydrogenation).

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11 Typical procedure for hydrodeoxygenation: Into a Teflon vessel were successively placed Pt/CsPW (Pt: 0.1 mol %), **1a** (0.5 mmol), heptane (1 mL), and a Teflon-coated magnetic stir bar. The Teflon vessel was attached inside an autoclave, and the reaction was carried out at 120 °C (bath temperature) in 5 atm of H_2. After the reaction was completed (3 h), an internal standard (naphthalene) was added to the reaction mixture, and the conversion of **1a** and the product yields were determined by GC analysis. As for the reuse experiment, Pt/CsPW was separated by filtration and washed with heptane. The retrieved Pt/CsPW was dried at room temperature prior to being used for the reuse experiment. The products (mainly alkanes) were confirmed by the comparison of their GC retention times and GC-MS spectra with those of authentic data.

12 Among the solvents examined, nonpolar solvents (e.g., heptane, mainly utilized in this study) were suitable for the hydrodeoxygenation of **1a**. In contrast, the desired deoxygenated product **2a** was hardly produced under the conditions described in Table 1 when using polar solvents such as DMF and diglyme.

13 The BET surface areas of CsPW and HPW were 142 and 4 $m^2 g^{-1}$, respectively.

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