Preferential catalytic hydrogenation of aromatic compounds *versus* ketones with a palladium substituted polyoxometalate as pre-catalyst

Letter

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A palladium-substituted polyoxometalate having a Keggin structure, supported on γ-alumina or active carbon, was used as a catalyst precursor for catalytic hydrogenation. The catalyst system enabled fast hydrogenation of arenes at 30 bar H_2 and 230 °C. Most interesting was the finding that arenes could be selectively reduced in the presence of distal ketone groups under similar conditions, 30 bar H_2 and 200 °C. For example, 1-phenyl-2-propanone yielded 1-cyclohexyl-2-propanone with no reduction of the ketone moiety. Additionally, aromatic compounds with *vicinal* (conjugated) ketone moieties underwent complete hydrogenation to saturated hydrocarbons and catalytic McMurry coupling was observed for aliphatic aldehydes.

The use of polyoxometalates as catalysts has become an important area of research over the past two decades. Most of the interest has been centered around the use of heteropoly acids in acid-catalyzed reactions[1] and the use of polyoxomolybdates and transition metal substituted polyoxometalates as catalysts for oxidation.[2] The use of polyoxometalates as catalysts in reductive transformations has been less explored. Some important examples do exist and include the use of Rh^0 and Ir^0 clusters stabilized by polyoxometalates for the hydrogenation of alkenes,[3] the reduction of nitroaromatics,[4] and the reductive deoxygenation of aldehydes and ketones.[5] Although the synthesis of various noble metal substituted polyoxometalates has been described,[6] surprisingly the simple use of these compounds in reductive transformations such as hydrogenation has not been reported. We have now found that a palladium-substituted Keggin-type polyoxometalate, supported on active carbon or γ-alumina, yields under hydrogen pressure a palladium(0) catalyst that shows catalytic activity and selectivity significantly different than those shown by the common supported Pd(0) catalyst Pd/C. This interesting selectivity is exemplified by: (a) the selective hydrogenation of aromatic rings to saturated cycloalkanes in the presence of distal ketone groups that remain unchanged under the reaction conditions; (b) the complete hydrogenation of aromatic compounds with *vicinal* ketone moieties to saturated hydrocarbons and (c) catalytic McMurry coupling observable for aliphatic aldehydes.

The palladium-substituted Keggin-type polyoxometalate formulated by elemental analysis as $K_5PPd(H_2O)W_{11}O_{39}\cdot 12H_2O$ was prepared in a manner similar to the published literature procedure for the preparation of $[(C_4H_9)_4N]_5PPd(H_2O)W_{11}O_{39}$.[7] The ^{31}P NMR spectrum (85% H_3PO_4 as external standard) revealed a major peak at −15.17 ppm (95%) attributable to $[PPd(H_2O)W_{11}O_{39}]^{5-}$ and/or possibly its dimer,[8] $[PW_{11}O_{39}Pd–O–PdPW_{11}O_{39}]$, and a small peak at −13.32 ppm (5%) attributable, from an authentic sample, to an impurity of the starting material, $[PW_{11}O_{39}]^{7-}$. The IR spectrum showed peaks at 1100, 1046, 950, 851, 805 cm^{-1}. Together, the elemental analysis and ^{31}P NMR reveal the formation of a rather pure compound as also previously published.[7] However, the IR spectrum, which is similar to the lacunary $Na_7PW_{11}O_{39}\cdot xH_2O$ compound (1101, 1043, 951, 858, 807 and 741 cm^{-1}), would seem to indicate that the Pd position is somewhat removed from the polyoxometalate framework but near the lacunary position.[9] This is not especially surprising since true framework substitution of Pd(II) into the polyoxometalate would require a less or non-preferred octahedral coordination for Pd(II), which generally adopts a square planar coordination. The lability of the palladium center was also verified by addition of cyclooctadiene to the $[PPdW_{11}O_{39}]^{5-}$ compound, which resulted in the demetalation of the polyoxometalate and formation of $[PW_{11}O_{39}]^{7-}$.

The supported pre-catalysts were prepared by wet impregnation with water of $K_5PPdW_{11}O_{39}\cdot 12H_2O$ (Pd-POM) onto active carbon and γ-alumina, yielding 10 wt % (Pd-POM)/C and 10 wt % (Pd-POM)/Al_2O_3. These catalysts were first tested in the hydrogenation of aromatic compounds, Table 1. As can be seen from the table, the (Pd-POM)/C catalyst is active for the complete hydrogenation of aromatic compounds to cycloalkanes at 30 bar H_2 and 230 °C. In difficult cases a slight increase in temperature has a positive effective on the reactivity. The catalysts were recycled three times by filtration and washing with dichloromethane without noticeable loss of activity.

Significantly, under the conditions described in the table, 1,2-octanone was *not* reduced either in the presence or absence of toluene, which itself was reduced to methylcyclohexane. This led to the possibility that compounds containing both an aromatic nucleus and ketone moiety could be hydrogenated selectively at the aromatic nucleus.[10] Therefore, a screening of hydrogenation of aromatic ketones is presented in Table 2. Under relatively harsh hydrogenation conditions (30 bar, 200 °C), the (Pd-POM)/C catalyst shows high selectivity for reduction of aromatic rings in the presence of *distal* ketone moieties, which remained unchanged, while simple aromatic ketones such as acetophenone and benzophenone were completely reduced. However, for the latter substrates hydrogenation under milder conditions (15 bar, 130 °C) showed initial reduction of the ketone to the methylene product and then hydrogenation of the aromatic ring. Interestingly, the commercial Pd/C catalyst shows significantly different reaction selectivity, leading to reduction of the aromatic ring to the saturated cycloalkane and the ketone moiety to the corresponding alcohol. With Pd/C ketone moieties are always reduced to alcohols while with (Pd-POM)/C distal or aliphatic ketones are not reactive and aromatic ketones are reduced or deoxygenated to the methylene moiety.

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Table 1 Hydrogenation of aromatic compounds catalyzed by $K_5PPdW_{11}O_{39}/C$ and $K_5PPdW_{11}O_{39}/Al_2O_3$[a]

Substrate	Product, selectivity/mol%	Conversion/mol%
Toluene	Methylcyclohexane, 100	100
Toluene[b]	Methylcyclohexane, 100	100
Durene	Hexahydrodurene, 100	100
Anthracene	Perhydroanthracenes, 93 Octahydroanthracenes, 7	100
Phenanthrene	Dihydrophenanthrene, 31 Tetrahydrophenanthrene, 16 Octahydrophenananthrene, 5	52
Phenanthrene[c]	Perhydrophenanthrenes, 99	100
Naphthalene	Tetralin, 67 Decalin, 33	100
Naphthalene[c]	Decalin, 100	100
Acridine	Perhydroacridine, 100	100

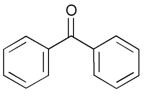
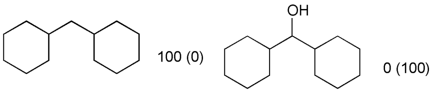
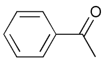
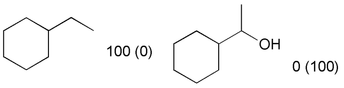
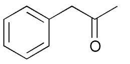
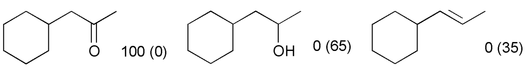
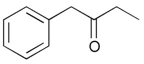
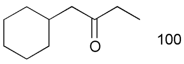
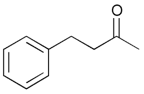
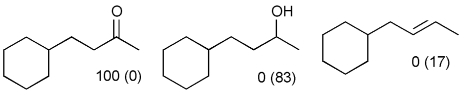
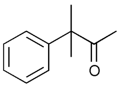
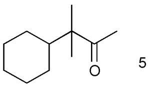
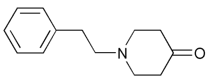
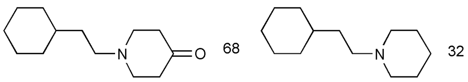
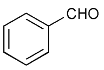
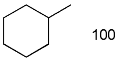
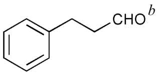
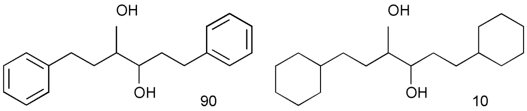
[a] Reaction conditions: 1.75 mmol substrate, 0.3 g 10 wt% $K_5PPdW_{11}O_{39}/C$, 1 mL pentadecane, 30 bar H_2, 230 °C, 1 h. [b] $K_5PPdW_{11}O_{39}/Al_2O_3$. [c] 230 °C, 4 h.

There are also significant steric effects in this reaction. For instance, 3-methyl-3-phenyl-2-butanone and also 3-phenyl-2-butanone (not shown in Table 2) are practically inert to the hydrogenation reaction. Apparently, the key interaction between the aryl nucleus and the palladium catalytic center is significantly hindered to prevent effective reduction of the carbonyl and aryl moiety. (Pd-POM)/Al_2O_3 and (Pd-POM)/C showed almost identical reactivity and selectivity. Also fascinating is the reduction of aromatic aldehydes. While hydrogenation of benzaldehyde yields methylcyclohexane, hydrogenation of dihydrocinnamaldehyde yielded only a catalytic McMurry coupling to the diol followed by some reduction of the aromatic rings. This represents a very significant change in the reaction pathway.

Finally, it is also worth noting that the (Pd-POM)/C catalyst is superior to the analogous compounds (Ru-POM)/C and (Rh-POM)/C, which were less reactive and less selective. Thus, for the reduction of 4-phenyl-2-butanone under the reaction conditions noted in Table 2, (Ru-POM)/C yielded 19% 4-cyclohexyl-2-butanone and 28% 4-phenyl-2-butanol and (Rh-POM)/C yielded 69% 4-cyclohexyl-2-butanone, 6% butenylcyclohexane and butylcyclohexene isomers and 3% cyclohexenyl-2-butanone and cyclohexadienyl-2-butanone.

Although we have no clear-cut understanding of the reaction selectivity observed, it was useful to carry out some studies on the supported catalyst after reaction or activation with hydrogen. Thus, an XPS measurement of the isolated "active" catalyst from the (Pd-POM)/Al_2O_3 precursor revealed Pd in zero oxidation state only.[11] On the other hand trituration of the active catalyst with water at 90 °C showed by ^{31}P NMR the extraction of the lacunary species, $PW_{11}O_{39}^{7-}$, into solution (peak at −13.25 ppm) and the absence of dissolved palladium

Table 2 Hydrogenation of aromatic ketones catalyzed by 10 wt% $K_5PPdW_{11}O_{39}/C$[a]

Substrate	Products
	 100 (0); 0 (100)
	 100 (0); 0 (100)
	 100 (0); 0 (65); 0 (35)
	 100
	 100 (0); 0 (83); 0 (17)
	 5
	 68; 32
	 100
 [b]	 90; 10

[a] Reaction conditions: 1.75 mmol substrate, 0.3 g 10 wt% $K_5PdW_{11}O_{39}/C$, 1 mL pentadecane, 30 bar H_2, 200 °C, 4 h. Yields in parentheses are those found when using commercial 10% Pd/C as catalyst. [b] 16 h.

(ICP analysis). TEM measurements show formation of small nanometric particles, ~2 nm diameter, on the alumina support, with EDS analysis showing the presence of both Pd and W. Therefore, we speculate that the active catalyst is possibly a Pd^0 cluster stabilized by the lacunary polyoxometalate species.[3] This combination of the Pd^0 cluster and polyoxometalate presumably leads to the unique hydrogenation selectivity observed, that is the significantly different reactivity observed for aliphatic ketones and aldehydes *versus* aromatic ketone and aldehydes. Notably, impregnation of the Pd/C catalyst with $Na_7PW_{11}O_{39}$ does not lead to this selectivity.

Experimental

The Pd-POM formulated as $K_5PPdW_{11}O_{39}\cdot 12H_2O$ was prepared by adding dropwise $PdCl_2$ (1.1 mmol, 200 mg) dissolved in 20 mL deionized water to a solution of $Na_7PW_{11}O_{39}\cdot xH_2O$ (1.0 mmol, 3.2 g) dissolved in 20 mL hot deionized water. After additional heating for 1 h at 90 °C a saturated solution of KCl (20 mL) was added and the solution was cooled. The brown precipitate was collected and recrystallized from water (yield 2.9 g, 90%). ICP elem. anal. exptal (calcd) K 5.86 (6.08), P 1.02 (0.96), Pd 3.12 (3.31), W 63.15 (62.94), H_2O 7.37 (7.29)%. Reactions were carried out in a 50 mL Parr autoclave under the conditions noted in the table captions. Analysis of the reactions were carried out by GC and GC-MS along with use of reference samples.

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