A Reusable Polymer-anchored Palladium Catalyst for Reduction of Nitroorganics, Alkenes, Alkynes and Schiff Bases†

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The preparation and utility of a new polymer-anchored Pd^{II} catalyst for the hydrogenation of a wide range of organic substrates is described.

Catalytic reduction[1] of organic compounds is an important process both in the laboratory and in industry, and continues to be the subject of active research. Methods based[2] on catalytic hydrogenation in homogeneous and heterogeneous media are commonly adopted for the hydrogenation of organic compounds. However, the reproducibility and selectivity of these methods, particularly of noble-metal-catalysed hydrogenation, has restricted their popularity. To improve upon the selectivity of a catalyst, we considered immobilization of a catalytic system. Immobilization of catalysts or reagents to polymer supports often offers many advantages for carrying out organic transformations.[3] Ease of work-up, higher yields, product selectivity and re-usability of the catalysts make them more attractive than their homogeneous counterparts. In the area of hydrogenation of organic substrates, extensive work has been performed on the development of Rh-based polymer supported catalysts.[4,5] Sometime ago we and others reported the use of a Pd^{II} homogeneous catalyst[6-9] for the reduction of a host of nitro-aromatics and -aliphatics. To develop its polymer-bound version, we have now prepared a synthetically useful Pd^{II} catalyst for reduction of functional groups like •NO$_2$, >C, C<, >C, N•, •C, C•, *etc.* in excellent yields. Catalyst **1** was readily accessible in two steps from aminopolystyrene[10] (Ⓟ-NH$_2$). Treatment of the polymer with PhCOR (R = H, Me, Ph) provided the corresponding Schiff bases, which were then treated with Pd^{II} acetate in acetic acid to yield catalysts **1** as dark brown solids (Scheme 1).

Characterization of **1** was performed by IR and ESCA. The ESCA peaks[11] at 338.25 eV (Pd 3d$_{5/2}$) and 343.75 eV (Pd 3d$_{3/2}$) and IR signals[6,12,13] at 1585, 1420 and 722 cm^{-1} indicate the presence of acetato-bridged orthometallated palladium(II) in catalyst **1**.

Catalysts **1** are activated by stirring them under H$_2$ (1 atm) at 80 °C for 1 h to produce the active species **2**. Chemical analysis indicates the presence of ∼12.25% of Pd in catalyst **2**. Characteristic ESCA signals, and IR signals at 722, 1985 (v_{Pd-H})[14,6] and 1655 cm^{-1} (v_{co}, DMF), confirm the structure **2**. Comparable ESCA and IR signals were also observed for the
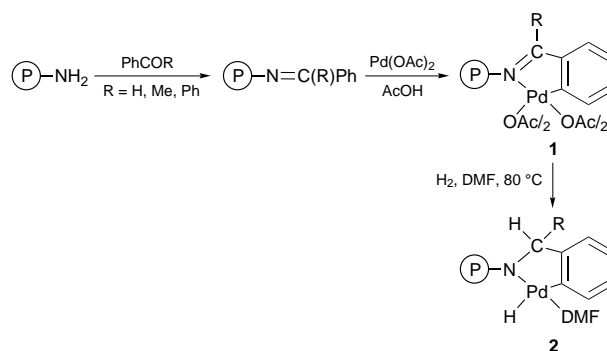
Scheme 1

used catalyst. Moreover, the Pd-content of the catalyst, as measured by gravimetric analysis, remained unchanged even after several cycles.

Exposure of an organic substrate in DMF–ethyl acetate medium containing catalyst **2** to hydrogen (1 atm) at room temperature resulted in rapid reduction of the substrate. As shown in Table 1, the reduction of nitroaromatics to amino-aromatics proceeds in excellent yields. In contrast, the reduction of nitroaliphatics (Table 3) requires higher temperatures (∼70 °C) and pressures (∼10.5 × 10^3 kN m^{-2}). However, the yields of the products were consistently excellent. Hydrogenation of double bonds of alkenes, alkynes and Schiff bases to their corresponding saturated products under normal conditions is more facile, ω-nitrostyrene being reducible to ω-nitroethylbenzene in excellent yield. Catalyst **2** when R = H is the most active. The results described in Tables 1–3 involve the use of this catalyst. It offers a high degree of chemoselectivity.

Hydrogenation of halonitroaromatics to the corresponding haloanilines is often accompanied by dehalogenation, and entails extensive optimization experiments.[1] This problem could be greatly obviated by the use of catalyst **1**. For example, a chloro substituent *ortho* or *para* to a nitro group remains intact. Similarly, a lactone (Tables 1 and 3, entry 7)

Table 1 Atmospheric pressure reduction of nitroaromatics

Entry	Substrate	Time t/h	Initial turnover no. min^{-1}	Product	% Yield
1	Nitrobenzene	3.5	2.30	Aniline	97
2	*o*-Nitrotoluene	6.25	1.22	*o*-Toluidine	90
3	*o*-Chloronitrobenzene	5.37	1.40	*o*-Chloroaniline	92
4	*p*-Chloronitrobenzene	4.9	1.70	*p*-Chloroaniline	94
5	*m*-Dinitrobenzene	7.0	1.00	*m*-Phenylenediamine	92
6	1-Nitronaphthalene	8.0	0.86	1-Aminonaphthalene	93
7	6-Nitrophthalide	8.5	0.80	6-Aminophthalide	94[b]
8	Methyl 4,5-dimethoxy-2-nitrobenzoate	8.5	0.79	Methyl 4,5-dimethoxy-2-aminobenzoate	92[b]

[a][sub] = 0.50 mol dm^{-3}, total vol. = 10 ml, medium = DMF; yields refer to GC analysis. [b]Isolated yield, [cat] = Pd content = 1.50 × 10^{-3} mol.

group is not affected under the conditions employed. The superiority of catalyst **2** is clearly discernible from entry 8 of Table 1, in which a methoxy substituted nitroester is shown to be reducible to its amine in high yield. It may be noted that

Table 2 Atmospheric pressure reduction of miscellaneous substrates[a]

Entry	Substrate	Time/h	Initial turnover no. min^{-1}	Product	% Yield
1	Hex-1-ene	1.2	7.0	Hexane, hex-2-ene	86, 12
2	Styrene	0.70	14.70	Ethylbenzene	98
3	ω-Nitrostyrene	1.4	5.80	ω-Nitroethylbenzene	95
4	Fumaric acid	2.8	3.00	Succinic acid	92
5	Isoprene	0.72	14.70	2-Methylbutane	97
6	Phenylacetylene	0.81	13.10	Ethylbenzene	97
7	Benzylideneaniline	1.96	4.30	N-Phenylbenzylamine	100
8	N-Methylbenzaldimine	1.5	5.60	N-Methylbenzylamine	100

[a][sub] = 0.50 mol dm^{-3}, reaction mixture vol. = 10 ml, medium = DMF.

Table 3 High pressure reduction of nitroaliphatics[a]

Entry	Substrate	Time (t/h)	Initial turnover no. min^{-1}	Products	% Yield
1	Nitroethane	6.2	3.56	Ethylamine	98
2	1-Nitropropane	6.5	3.33	1-Aminopropane	97
3	2-Nitropropane	7.2	2.93	2-Aminopropane	96
4	1-Nitroheptane	6.8	3.11	1-Aminoheptane	94
5	ω-Nitroethylbenzene	7.0	2.99	ω-Aminoethylbenzene	95
6	Acetonitrile	8.6	2.12	Diethylamine	93
7	Phthalic anhydride	8.5	1.58	Phthalide	86[b]

[a]Medium = DMF, [sub] = 1.50 mol dm^{-3}, total vol. = 10 ml; [b]isolated yield, [cat] = 1.70×10^{-3} g·atom dm^{-3}, $p_{H2} = 10.5 \times 10^{-3}$ kN m^{-2}, $T = 70\ ^\circ$C.

conventional hydrogenation of nitroesters over Pd or Pd/C provides variable yields of the corresponding amine.[15]

Although the described use of the catalyst **2** in the reduction of various organic substrates is quite general, it involves a restricted choice of reaction media. It appears that DMF is the best solvent for such reactions though hydrogenation occurs in ethyl acetate at a slower rate. The remarkable advantages with the use of the catalyst **2** are the ready accessibility of the catalysts, their reusability and storage. Even after recycling 7 or 8 times, the catalyst retains its original activity. Furthermore, the used catalysts are free from fire hazards or explosions. They can be used for selective reduction of an aromatic nitro group in the presence of an aliphalic nitro group, under atmospheric pressure, as evident from Tables 1 and 3. Further studies on product selectivity are under way.

Experimental

In a typical procedure, a solution of a substrate (5.0 mmol) in DMF (10 ml) containing the catalyst **2** (14.0 mg) was subjected to hydrogenation under hydrogen (1.0 atm) in a magnetically stirred glass reactor. The rate of hydrogen consumption was measured using a glass manometric apparatus. The detailed experimental set-up and hydrogenation procedure have been described earlier.[8] After the completion of the reaction, the catalyst was filtered off and the filtrate analysed by GC. In certain cases the products were isolated by usual work-up followed by preparative tlc.

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