Demonstration of a Novel Method for the Controlled Deposition of Metals onto Surfaces by Preparation of a Pd–Hg/SiO_2 Catalyst for the Selective Hydrogenation of Alkynes to Alkenes

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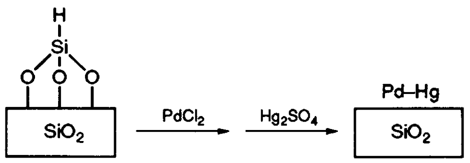
Treatment of silica gel that has SiH functional groups bonded to the surface, with methanolic $PdCl_2$ and then aqueous Hg_2SO_4 affords a new catalytic material for the chemo- and stereo-selective partial hydrogenation of alkynes to *Z*-alkenes with a high degree of functional group compatibility.

Supported catalysts are commonly prepared by a variety of techniques that include precipitation of metals onto support materials through the reduction of salts from solution, reduction of crystals of metallic salts deposited on the surface following precipitation or solvent evaporation, or by chemical vapour deposition.[1] It is often difficult to control catalyst metal crystallite size, concentration and distribution on the support using these techniques. Superior control of metal deposition offers the possibility of improved catalytic properties better tailored for individual purposes. This can be accomplished by fixing chemical reducing centres on the support prior to the introduction of metal ions. The pre-establishment of such sites thus determines the concentration and distribution of the metals ultimately deposited on the surface.

Compounds containing the silyl hydride (SiH) functionality can reduce salts of many metals to the corresponding elemental metals.[2] Recently, we have established that each SiH group represents a one-electron reduction site for aqueous metallic ions [eqn. (1)].[3] The immobilization of silyl hydride functions onto existing surfaces and the characterization and reactivity of the resulting materials have been reported.[3,4] We now demonstrate that through a two-step procedure we can utilize the reducing properties of such a pre-established surface for the novel preparation of a supported palladium catalyst partially poisoned with mercury that is selective for the hydrogenation of alkynes to *Z* alkenes and which is compatible with a number of other reducible functional groups.

$$n{\equiv}SiH + 2nH_2O + M^{n+} \rightarrow n{\equiv}SiOH + nH_3O^+ + n/2H_2 + M^0 \quad (1)$$

This preparation was carried out by the reduction of solutions of $PdCl_2$ and Hg_2SO_4 on the surface of silica gel having pre-existing surface-immobilized silyl hydride functions [eqn. (2)].†



(2)

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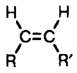
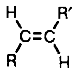
† The catalyst was prepared as follows: silica gel-immobilized silyl hydride (1.0 g, 2.0 mmol of SiH)[3] was added to 40 ml of methanolic solution containing a deficiency of $PdCl_2$ (0.010 g, 0.056 mmol). A black surface colouration immediately formed, indicating that the silyl hydride on the surface of the silica gel had reduced Pd^{2+} to Pd metal. Following stirring at room temp. for 24 h, the reaction mixture was filtered and the solid washed with 50 ml of methanol. An excess of sodium borohydride was added to the filtrate to reduce dissolved palladium ion until the yellow colour of the filtrate disappeared. Precipitated palladium metal was centrifgued in a pre-weighed centrifuge tube, washed repeatedly with methanol (5 × 20 ml), and then dried under vacuum and weighed. From this was calculated the mass of the palladium metal dispersed on the silica gel (0.3% w/w). This material was then added to an aqueous mercury(I) sulfate solution [1.2 mg of mercury(I) sulfate dissolved in 50 ml of distilled water]. The reaction mixture was stirred for 7 h at room temp., then filtered and the solid washed with 100 ml of distilled water followed by 100 ml of methanol. The catalyst was dried first on a Büchner funnel for 2 h under aspirator vacuum and then in an oven at 75 °C for 4 h.

Table 1 Hydrogenation of alkynes to alkenes using Pd–Hg/SiO_2 catalyst[a]

Substrate	t/h	Products, yield (%)[a]		
R-C≡C-R′				$R-CH_2-CH_2-R'$
R = R′ = Ph	4	85[b]	3[b]	12[b]
R = Ph; R′ = H	10	93[b,c]	—	7[b,c]
R = R′ = Pr^n	6	97[c–e]	—	—
R = R′ = MeO_2C	2	95[b,d]	3[b,d]	2[b,d]
R = R′ = $HOCH_2$	16	92[f,g]	—	—
R = Et R′ = $C_2H_4OCH_2Ph$	12	87[d]	—	—

[a] All reactions were run in hexane (15 ml) at room temp. under 1 atm of H_2 using *ca.* 0.50 mmol of substrate and 50 mg of catalyst unless otherwise indicated. [b] Determined by ^1H NMR. [c] Determined by GC. [d] Determined by GC–MS. [e] Determined by ^{13}C NMR. [f] Isolated. [g] Ethyl acetate used as solvent.

Following preparation of the catalyst, its efficacy was tested by the partial hydrogenation of several acetylenic compounds at room temperature under 1 atm of H_2 (Table 1).‡ This catalyst was found to be superior to some of the other reported catalysts (Pd/C[5] and cationic Rh complex[6]) for the partial hydrogenation of butyn-1,4-diol. This catalyst was also selective for the hydrogenation of an alkyne in the presence of a benzyl ether functionality.[7] It has been reported that the rates of hydrogenation of an alkyne to an alkene and an azide to an amine are almost the same with the Lindlar catalyst.[8] In contrast to this behaviour, competitive hydrogenation of an equimolar mixture of dodecyl azide and dimethyl acetylene dicarboxylate in the presence of this Pd–Hg/SiO_2 catalyst yielded only dimethyl maleate (a *Z* isomer) and unchanged dodecyl azide. Also, competitive hydrogenations of oct-4-yne in the presence of either cyclohexylmethyl bromide or *m*-nitroacetophenone resulted only in the selective reduction of the alkyne to (*Z*)-oct-4-ene. Neither alkyl halide nor aromatic nitro group were affected.

In conclusion, we have demonstrated a novel two-step technique for the preparation of catalytic materials by controlled deposition of metals onto surfaces of existing materials. We believe this method should be applicable to a wide range of substrate materials and deposited metals. In preliminary studies, we have used this method to deposit a number of metals on surfaces of silica, alumina, titania and common glass and are presently studying the properties of the resulting new materials.[9]§

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‡ Exposure of the silica gel-immobilized silyl hydride to an excess of methanolic $PdCl_2$ gave a black material with very strong catalytic properties that caused the rapid hydrogenation of diphenylacetylene to bibenzyl.

§ We have confirmed by energy dispersive X-ray analysis the presence of a number of metals deposited in this way on silica and titania surfaces. Preliminary element mapping observations indicate that the metals are widely dispersed across the surface rather than being concentrated in well-defined large crystallites, as is the case in some commercially available supported catalysts we have examined. We are continuing our studies to define better the surface properties of these new materials.