LETTER

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Hydrogenation *versus* hydrogenolysis with a safe, selective and reusable catalyst: palladium black on Teflon®

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Palladium black deposit is obtained by reduction and metallization of the Teflon® polymer surface of magnetic stirring bars. These stirring bars can be used to perform selective hydrogenation of olefins and acetylenic compounds whilst hydrogenolysis is not observed.

The classical heterogeneous catalysts for carbon–carbon multiple bond hydrogenation involve supported precious metals, activated base metal catalysts and Ni supported on oxides, all being able to activate hydrogen under mild conditions. Due to its chemoselectivity, Pd is the most widely used catalyst compared to other Group VIII transition metals, Pt, Rh, Ru and Ni. Several excellent reviews dealing with the catalytic hydrogenation of carbon–carbon multiple bonds have appeared in the last few years, providing comprehensive information on the subject.[1–6]

Palladium catalysts, such as palladium black or palladium on carbon (Pd/C), are mainly used to reduce alkenes and alkynes to their corresponding hydrocarbons,[7] they can also be used to achieve the hydrogenolysis of halides,[8] benzyl ethers, benzylamines[9] and to convert cyclopropanes to *gem*-dimethyl compounds.[10] Even if the hydrogenation process is a clean and easily implementable process, the palladium catalyst is flammable and dry Pd/C catalyst must be handled carefully. The danger of ignition is always present due to the electrical discharge caused by friction when palladium is placed in a reaction mixture. Even if the hydrogenation and the hydrogenolysis are different reactions, the differentiation between these two reactions is difficult as the experimental conditions are the same. If different methods for selective hydrogenation without hydrogenolysis have been reported, catalysts with selective activity based on their preparation are very rare.[11]

Here, we would like to report that a Teflon® magnetic stirring bar with a deposit of palladium black (Pd/TMSB) is an easily handled, non-flammable catalyst, easy to remove from the reaction media. This catalyst can be used in the hydrogenation of olefins and alkynes and is highly chemoselective as it can not perform the hydrogenolysis of cyclopropanes, benzyl ethers and allylamines. Furthermore, no trace of the catalyst remains in the solution when Pd/TMSB is used (Scheme 1).

Chemical modification of Teflon® [poly(tetrafluoroethylene), PTFE] by organic moieties or by metals such as Au, Ag and Cu has already been reported in the case of Teflon® plates.[12] At first the plates were reduced locally in the vicinity or at the contact of a disc electrode biased at a sufficiently negative potential.[13] Then, the reduced zones were reacted with a diazonium or a metallic salt. This led to the localized grafting of the organic moiety derived from the diazonium salt or to localized electroless metallization. This process takes advantage of the *n*-doped character of polymeric carbon obtained when Teflon® is reduced.[14]

We have performed metallization with palladium according to a two-step procedure deduced from that used for Au, Ag and Cu plates.[12b] A Teflon® coated stirring bar was reduced upon contact with a stainless steel wire in the presence of 2,2′-dipyridyl (P) in DMF. The wire was biased at a more negative potential than the reduction potential of 2,2′-dipyridyl ($E^\circ = -2.10$ V *vs.* saturated calomel electrode) in order to generate the 2,2′-dipyridyl radical-anion ($P + e^- \rightarrow P^{\bullet -}$). This procedure led to the carbonization and the *n*-doping of Teflon® according to eqns. (1) and (2) respectively, in which NBu_4^+ is the cation of the electrolyte:

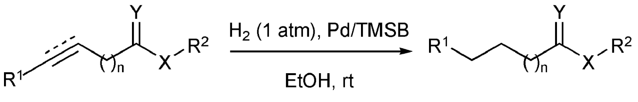
$$-(\mathrm{CF_2})-_n + 2ne^- + 2n\mathrm{NBu_4^+} \longrightarrow -(\mathrm{C})-_n + 2n(\mathrm{NBu_4^+F^-}) \qquad (1)$$

$$-(\mathrm{C})-_n + \delta n\mathrm{NBu_4^+} + \delta ne^- \longrightarrow [-(\mathrm{C}^{-\delta})-_n, \delta n\mathrm{NBu_4^+}] \qquad (2)$$

In eqn. (1), the electron (e^-) is either provided by the electrode or the radical-anion of 2,2′-dipyridyl. The latter acts as a reducing agent, especially in the places where there is bad contact between the wire and the Teflon® magnetic stirring bar. The solution was electrolyzed under potentiostatic conditions ($V_{\mathrm{ref}} - V_{\mathrm{stirrer}} = 2.5$ V) for 400 s. The reduction resulted in the development of a black carbonized zone (2–3 mm wide) around the stainless steel wire. Secondly, the modified Teflon® bar was reacted with a palladium salt. The latter was reduced spontaneously by the negatively charged Teflon® [eqn. (3)], which resulted in the metallization of the Teflon® bar:

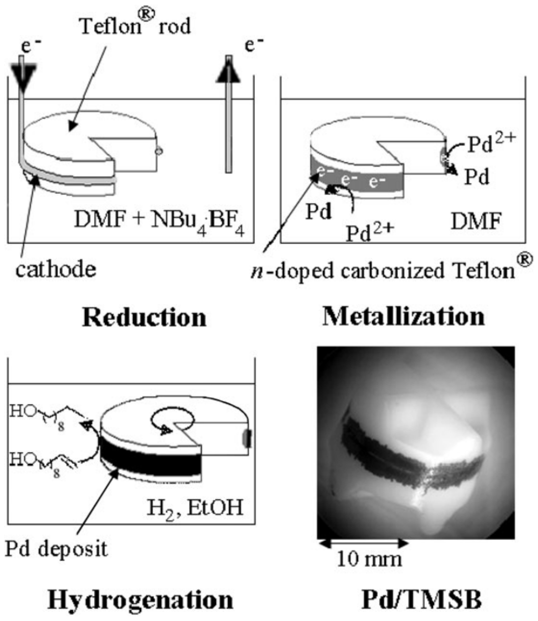
$$\mathrm{Pd^{2+}} + 2/\delta n[-(\mathrm{C}^{-\delta})-_n, \delta n\mathrm{NBu_4^+}] \longrightarrow \mathrm{Pd} + 2/\delta n-(\mathrm{C})-_n + 2\mathrm{NBu_4^+} \qquad (3)$$

The complete process is presented in Scheme 2. Using X-ray fluorescence, metallization was confirmed by the appearance of the characteristic system of Pd at about 3 × 10³ eV (Fig. 1).



R^1 = H, Alkyl, Aryl ; R^2 = H, Benzyl ; X = O, NBoc ; Y = O, H_2

Scheme 1 Hydrogenation of olefins and alkynes using Pd/TMSB.



Scheme 2 Carbonization and metallization of a Teflon® coated stirring bar and optical micrograph of Pd/TMSB.

The amount of deposited palladium, measured by inductive coupling plasma-mass spectrometry (ICP-MS), was approximately 4.8 μg for 60 mm^2 and corresponds to an average deposit thickness of ~7 nm.

The Pd/TMSBs were tested in the hydrogenation of olefins. A typical hydrogenation was achieved as follows: an ethanolic solution (5 mL) of **1** (1 mmol) containing a Pd/TMSB was stirred by the Pd/TMSB itself under one atmosphere of hydrogen at room temperature. After 17 h, the Pd/TMSB was removed with a magnetic stick and the solution was concentrated under vacuum to give **2** in quantitative yield with a purity superior up to 98% without any additional purification. The Pd/TMSB could be recycled after washing with EtOH and drying under vacuum. The Pd/TMSB could be used four times in the hydrogenation of **1** without any loss of activity as **2** was obtained in yields superior to 98%. After the fifth run, the yield in **2** was identical but the hydrogenation of **1** had to be performed for 40 h (Table 1). It is worth noting that no trace of palladium was detected in the hydrogenation solutions (by ICP-MS analysis).[15]

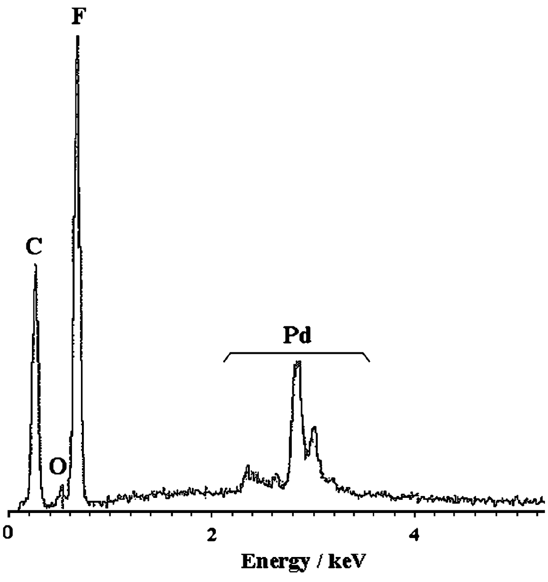
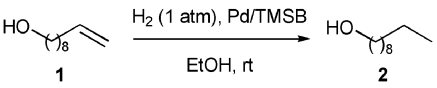


Fig. 1 X-Ray fluorescence spectrum of a Teflon® coated stirring bar after carbonization and metallization.

Table 1 Recovery and reuse of Pd/TMSB



1 → **2**

Run	1	2	3	4	5
Time (h)	20	20	20	20	40
Yield (%)	>98	>98	>98	>98	>98

The hydrogenation of alkenes in the presence of the Pd/TMSB catalyst is general and the results are reported in Table 2. Terminal olefins without or with polar substituents such as hydroxy groups can be hydrogenated in good yields (>80%) (Table 2, Entries 1–3). However, 1,3-diol **5** was recovered unchanged. The presence of the two hydroxy groups is probably responsible for the deactivation of the Pd/TMSB due to a chelating effect (Table 2, Entry 4).

The hydrogenation of the benzyl protected but-3-en-1-ol **6** led to benzyloxybutane **18** and to compound **18′** in a ratio of 70 : 30 and with a global yield of 95%. Compound **18′** corresponds to the migration of the double bond.[16] Under these conditions, the benzyl group was not cleaved (Table 2, Entry 5).

In the case of *N*-Boc-*N*-benzylallylamine **7**, the hydrogenation did not lead to the corresponding deprotected amine but to the saturated amine **19**, still protected by the benzyl group, in quantitative yield (Table 2, Entry 6). Disubstituted double bonds were also hydrogenated as (*E*)-alkene **8** and (*Z*)-alkenes **9** and **10** were transformed easily and respectively to the corresponding saturated products **2**, **20** and **21** in good yield (Table 2, Entries 7–9). As previously observed, benzyl protecting groups were not cleaved (Table 2, Entry 9). Furthermore, activated olefins, such as α,β-unsaturated esters, can be hydrogenated easily as **11** was transformed to **22** in high yield (Table 2, Entry 10). However, disubstituted olefins with polar nucleophilic groups such as carboxylic groups were unreactive to hydrogenation. For example, cinnamic acid **12** and hept-6-enoic acid **13** were recovered unchanged due, maybe, to a coordination of the carboxylic acid to the palladium surface, which prevents the double bond from reaching the surface for hydrometallation (Table 2, Entries 11 and 12). The hydrogenolysis of cyclopropanes and hydrogenation of trisubstituted olefins were not observed when Pd/TMSB was used under these experimental conditions (Table 2, Entries 13 and 14). It is worth noting that, with classical Pd/C, the hydrogenation of **10** and **11** leads to the reduction of the double bond, as expected, but also to the deprotection of the alcohol.

The hydrogenation of acetylenic compounds was also achieved and the results are summarized in Table 3. The hydrogenation of **23**, **24** and **25**, in the presence of a Pd/TMSB, under one atmosphere of hydrogen, led respectively to the corresponding saturated compounds **2**, **26** and **27** in quantitative yields (Table 3, Entries 1–3).

In conclusion, palladium black deposit on a Teflon® magnetic stirring bar (Pd/TMSB) promotes the hydrogenation of terminal and disubstituted olefins as well as acetylenic compounds in good yields when the reaction is performed under one atmosphere of hydrogen. The Pd/TMSB is easy to use, reusable and leaves no trace of residual palladium in the solution. Moreover, the deposition of the catalyst on a stirring bar allows the use of a high mass transfer rate, provided by the stirring bar rotation rate, toward the catalyst. This should be beneficial for the kinetics of classical Pd/solvent/H$_2$ hydrogenation processes. Furthermore, Pd/TMSB exhibits high selectivity as trisubstituted olefins and α,β-unsaturated carboxylic acids are not hydrogenated and the hydrogenolysis of benzyl ethers, benzylamines and deprotection of allylamines

Table 2 Hydrogenation of alkenes with Pd/TMBS

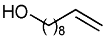
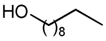
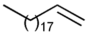
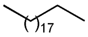
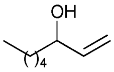
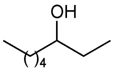
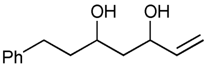
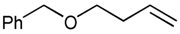
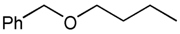
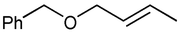
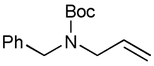
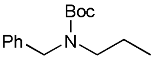
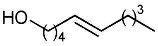
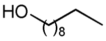
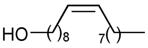
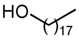
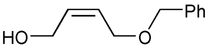
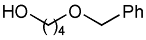
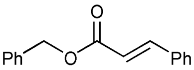
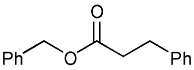
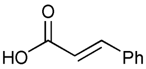
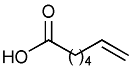
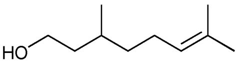
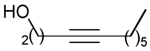
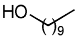
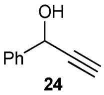
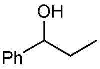
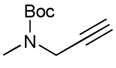
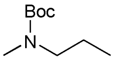
Entry	Starting materials	Time (h)	Products	Yield (%)
1	 **1**	17	 **2**	>98
2	 **3**	16	 **16**	>98
3	 **4**	20	 **17**	82
4	 **5**	40	—	—
5	 **6**	40	 **18/18'** (70/30) 	95
6	 **7**	30	 **19**	>98
7	 **8**	20	 **2**	95
8	 **9**	42	 **20**	91
9	 **10**	22	 **21**	78
10	 **11**	24	 **22**	>98
11	 **12**	24	—	—
12	 **13**	20	—	—
13	 **14**	20	—	—
14	 **15**	20	—	—

Table 3 Hydrogenation of alkynes

Entry	Starting materials	Time (h)	Products	Yield (%)
1	 **23**	20	 **2**	>98
2	 **24**	20	 **26**	>98
3	 **25**	20	 **27**	>98

are not observed. This effect does not result from any specific chemical property of Teflon®, which is well-known for its inertness.[14] It is likely due to the Pd deposition process and should be related to the specific physico-chemical properties of the *n*-doped carbonized PTFE: Pd deposition is achieved according to a redox process at an *n*-doped material surface of considerable roughness.

Experimental

Preparation of the Pd/TMSB

The magnetic stirring bars used are double cross-head cylinders and before treatment they are rinsed with acetone under sonication for 5 min and dried in an oven overnight (80 °C). In the first step, the cylindrical part of the Teflon® magnetic stirring bar is surrounded with a stainless steel wire (diameter: 1 mm) acting as a working electrode. The magnetic stirring bar and the wire are immersed into a solution of DMF containing tetrabutylammonium tetrafluoroborate (0.1 M, supporting electrolyte) and 2,2′-dipyridyl (10 mM, reducing agent precursor). The solution also contains a platinum wire (diameter: 1 mm) as a counter-electrode and an Ag/AgCl reference electrode. After reduction, the solution used for the Teflon® reduction is immediately replaced by a 10 mM solution of 2 $Na^+PdCl_4^{2-}$ in DMF for 2 h.

A Leo Stereoscan 440 scanning electron microscope (SEM B), operating at 20 keV, was used (Princeton Gamma-Tech). The coating system was a carbon coater Cressington 208 (ELOISE).

Hydrogenation using Pd/TMSB

A Pd/TMSB was introduced into a solution of an unsaturated compound (1 mmol) in absolute ethanol (5 mL). The solution was then stirred with the Pd/TMSB under one atmosphere of hydrogen for around 20 h (GC/MS monitoring). The Pd/TMSB was removed with a stick, washed with absolute ethanol and dried *in vacuo* for further experiment. The resulting solution was evaporated and the obtained product was purified by flash chromatography if necessary.

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