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# A New Class of Heterogeneous Platinum Catalysts for the Chemoselective Hydrogenation of Nitroarenes

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This article is dedicated to Francesco (“Ciccio”) Vinci, now a grandfather, for all he has donated to one of us (M.P.) and classmates in all these years.

**Abstract:** A new series of nanostructured platinum catalysts able to catalyze the selective reduction of nitroarenes has been developed. The materials, made of organosilica physically doped with nanostructured platinum(0), are stable and efficient. Reactions in general proceed with high yield and often go to completion, while the catalysts can be reused in further

reaction runs. This establishes a new class of relevant solid catalysts for synthetic organic chemistry named *SiliaCat* Platinum-Hydrogel.

**Keywords:** chemoselectivity; heterogeneous catalysis; hydrogenation; nanoparticles; nitroarenes; reduction; supported catalysts

## Introduction

Functionalized anilines are important intermediates for pharmaceuticals, polymers, dyes, urethanes and other industrially important chemical products.<sup>[1]</sup> Simple aromatic amines are generally obtained by catalytic hydrogenation of nitroarene compounds with various heterogeneous commercial catalysts (supported nickel, copper, cobalt) including Pt/C.<sup>[2]</sup> Yet, the selective reduction of a nitro group with H<sub>2</sub> when other reducible groups are present in the same molecule is generally not feasible with these catalytic materials, and requires the employment of advanced heterogeneous catalysts such as the doped Pt mediator introduced by Blaser and co-workers for the chemoselective hydrogenation of a chlorinated allylnitrobenzoate to the corresponding aniline.<sup>[3]</sup>

Following a decade of intense research, several heterogeneous catalysts for chemoselective hydrogenation of functionalized nitroarenes are currently commercially available.<sup>[4]</sup> In general, widely differing reaction conditions are used but very few (multicomponent) catalysts are able to catalyze the reduction at room temperature and under low (1 bar) hydrogen pressure. In brief, according to state of the art identified by Corma and co-workers in 2009, supported Pt catalysts are *not* chemoselective mediators for the reduction of nitro groups.<sup>[5]</sup> This emphasizes the relevant fundamental and applicative interest of the dis-

covery reported herein concerning the chemoselective catalytic activity of new Pt(0) heterogeneous catalysts for the hydrogenation reaction of a series of substituted nitro compounds under remarkably mild conditions, namely at room temperature with 1 bar H<sub>2</sub> in a simple hydrogen balloon, using a modest 0.5 mol% catalyst amount.

In brief, highly dispersed platinum nanoparticles entrapped within an organosilica matrix were successfully prepared by a novel and simple sol-gel route. In the new procedure, Pt nanoparticles uniformly in the range 1.7–3.15 nm are encapsulated *via* an alcohol-free sol-gel process typical of enzyme sol-gel encapsulation.<sup>[6]</sup> Trademarked **SiliaCat Pt<sup>0</sup>-Hydrogel**, this new series of sol-gel entrapped Pt nanocatalysts is now commercially available.

## Results and Discussion

### Solvent Effect

A series of different *SiliaCat* Pt<sup>0</sup> catalysts (Table 1) was prepared by changing the synthetic conditions as described in the Experimental Section.

The catalysts summarized in Table 1 were first tested in the selective reduction of 4-chloronitrobenzene to 4-chloroaniline to study the influence of the solvent on the catalytic process *or* on the hydrogena-

**Table 1.** Textural properties, load and preparation parameters of SiliaCat Pt<sup>0</sup>-Hydrogel catalysts.

Entry	Pt loading [mmol g <sup>-1</sup> ]	Surface area [m <sup>2</sup> g <sup>-1</sup> ]	Pore size [Å]	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]	MTES:K <sub>2</sub> PtCl <sub>4</sub> :H <sup>+</sup> :H <sub>2</sub> O <sub>total</sub> :NaOH (equiv.)
SiliaCat Pt <sup>0</sup> -1	0.05	493	42	0.72	1:0.004:0.003:8.56:0.023
SiliaCat Pt <sup>0</sup> -2	0.1	519	56	0.84	1:0.009:0.003:9.45:0.033
SiliaCat Pt <sup>0</sup> -3	0.2	502	60	0.88	1:0.018:0.003:11.97:0.053

**Table 2.** Influence of the solvent on catalytic activity and selectivity of SiliaCat Pt<sup>0</sup>-Hydrogel catalyst in selective reduction of 4-chloronitrobenzene.

Entry	Catalyst <sup>[a]</sup> (mol%)	Time [h]	Solvent	Product	Yield [%] <sup>[b]</sup>	
					Aniline	Other
1	SiliaCat Pt <sup>0</sup> -1 (1 mol%)	0.5	MeOH (0.1 M)	90	10	0
2	SiliaCat Pt <sup>0</sup> -2 (1 mol%)	0.5	MeOH (0.1 M)	92	8	0
3	SiliaCat Pt <sup>0</sup> -3 (1 mol%)	1	MeOH (0.1 M)	88	12	0
4	SiliaCat Pt <sup>0</sup> -1 (0.5 mol%)	1	MeOH (0.1 M)	95	5	0
5	SiliaCat Pt <sup>0</sup> -2 (0.5 mol%)	0.5	MeOH (0.1 M)	87	13	0
6	SiliaCat Pt <sup>0</sup> -3 (0.5 mol%)	1	MeOH (0.1 M)	73	27	0
7	SiliaCat Pt <sup>0</sup> -2 (0.5 mol%)	4	EtOAc (0.1 M)	55	0.5	0
8	SiliaCat Pt <sup>0</sup> -2 (1 mol%)	4	EtOAc (0.1 M)	75	1	0
9	SiliaCat Pt <sup>0</sup> -2 (2 mol%)	4	EtOAc (0.1 M)	90	1.5	0
10	SiliaCat Pt <sup>0</sup> -2 (0.5 mol%)	1	hexane (0.1 M)	71	10	19
11	SiliaCat Pt <sup>0</sup> -2 (1 mol%)	1	hexane (0.1 M)	50	11	29
12	SiliaCat Pt <sup>0</sup> -2 (0.5 mol%)	1	THF (0.1 M)	30	15	0
13	SiliaCat Pt <sup>0</sup> -2 (1 mol%)	1	THF (0.1 M)	45	17	0

<sup>[a]</sup> Experimental conditions: 2 mmol substrate in 20 mL MeOH solvent (HPLC grade) and mol% catalyst as specified in each Table entry, under hydrogen balloon/room temperature conditions.

<sup>[b]</sup> Determined by GC/MS analysis.

tion products (Table 2) using methanol, ethyl acetate, tetrahydrofuran, and hexane. Best results were obtained in HPLC grade methanol solvent (0.1 M concentration with respect to substrate). Even if the employment of EtOAc results in high selectivity, the reaction times are generally much longer. In hexane by using 0.5 or 0.1 mol% catalyst, complete conversion was obtained after 1 h, but the selectivity to 4-chloroaniline was generally low (selectivity = yield/conversion × 100).

### Catalytic Activity

The same substrate 4-chloronitrobenzene was also used to assess the catalytic activity of the materials prepared in Table 1. Results in Table 3 show that the hydrogenation reaction proceeds with full conversion for all three catalysts, over 0.5–0.1 mol% Pt nanostructured solid catalyst, after 0.5–2 h. Best results were obtained for the SiliaCat Pt<sup>0</sup>-2 catalyst (entries 6–10).

### Comparative Catalytic Activity

Other commercially available Pt heterogeneous catalysts [Pt/C, Pt/SiO<sub>2</sub> and Pt(0)EnCat40] were tested in

the selective reduction of 4-chloronitrobenzene under the same conditions identified for our best catalyst SiliaCat Pt<sup>0</sup>-2. The results in Table 4 show that the selective reduction of 4-chloronitrobenzene with Pt(0)/C heterogeneous catalyst (entries 1–3) is not complete after 1 h even over high amounts (5 mol%) of catalyst. If a 0.5 mol% catalyst amount is used, conversion after 1 h is 79% with disappointingly low selectivity.

When the Pt/SiO<sub>2</sub> is used (entries 4–6) conversion after 1 h is complete employing 5 mol% catalytic amount, but requires 2 h over 1 mol% catalyst. If a 0.5 mol% catalyst amount is used, conversion after 2 h is limited to 60%. Finally, when the Pt(0)EnCat40 (40% humidity) is applied in the reaction (entries 7–9), full conversion of 4-chloronitrobenzene was achieved after 1 h over 5 mol% Pt catalyst, and after 2 h over 1 mol% Pt. Again, if a 0.5 mol% catalyst amount is used (entry 9), conversion after 2 h is 75% with low selectivity to 4-chloroaniline.

The Pt<sup>0</sup>EnCat40 catalyst (Pt microencapsulated in polyurea)<sup>[7]</sup> was also tested after drying (entries 10–12). Now, complete transformation of 4-chloronitrobenzene was obtained over 5 mol% Pt after 0.5 h only, and after 2 h over 0.5–1 mol% Pt. In each reaction, however, when conversion is complete the amount of aniline was higher than 10%, even if now

**Table 3.** Catalytic reactivity of SiliaCat Pt<sup>0</sup>-Hydrogel catalyst in selective reduction of 4-chloronitrobenzene.<sup>[a]</sup>

Entry	Catalyst <sup>[b]</sup> (mol%)	Time [h]	Yield [%] <sup>[c]</sup>		
			4-Chloroaniline	Aniline	Other
1	SiliaCat Pt <sup>0</sup> -1 (5 mol%)	0.5	95	5	0
2	SiliaCat Pt <sup>0</sup> -1 (1 mol%)	0.5	90	10	0
3	SiliaCat Pt <sup>0</sup> -1 (0.5 mol%)	1	95	5	0
4	SiliaCat Pt <sup>0</sup> -1 (0.2 mol%)	1	86	14	0
5	SiliaCat Pt <sup>0</sup> -1 (0.1 mol%)	2	83	17	0
6	SiliaCat Pt <sup>0</sup> -2 (5 mol%)	0.5	96	4	0
7	SiliaCat Pt <sup>0</sup> -2 (1 mol%)	0.5	92	8	0
8	SiliaCat Pt <sup>0</sup> -2 (0.5 mol%)	0.5	88	12	0
9	SiliaCat Pt <sup>0</sup> -2 (0.2 mol%)	1	84	13	0
10	SiliaCat Pt <sup>0</sup> -2 (0.1 mol%)	2	90	10	0
11	SiliaCat Pt <sup>0</sup> -3 (1 mol%)	1	88	12	0
12	SiliaCat Pt <sup>0</sup> -3 (0.5 mol%)	1	73	27	0

<sup>[a]</sup> Experimental conditions: 2 mmol substrate in 20 mL MeOH solvent (HPLC grade), under hydrogen balloon/room temperature conditions.

<sup>[b]</sup> Catalyst identified in Table 1.

<sup>[c]</sup> By GC/MS analysis.

**Table 4.** Catalytic reactivity of different other Pt heterogeneous catalysts such Pt/C, Pt/SiO<sub>2</sub> and Pt<sup>(0)</sup>EnCat<sup>TM</sup>40 in selective reduction of 4-chloronitrobenzene.<sup>[a]</sup>

Entry	Catalyst	Catalyst (mol%)	Time [h]	Yield <sup>[b]</sup> [%]			
				Total conv.	4-Chloroaniline	Aniline	Other
1	Pt/C	5	1	98	82	14	2
2	Pt/C	1	1	94	65	4	25
3	Pt/C	0.5	1	79	43	0	36
4	Pt/SiO <sub>2</sub>	5	1	100	84	13	3
5	Pt/SiO <sub>2</sub>	1	2	100	88	10	2
6	Pt/SiO <sub>2</sub>	0.5	2	60	48	2	9
7	Pt <sup>(0)</sup> EnCat <sup>TM</sup> 40 wet	5	1	100	75	18	7
8	Pt <sup>(0)</sup> EnCat <sup>TM</sup> 40 wet	1	2	100	78	14	8
9	Pt <sup>(0)</sup> EnCat <sup>TM</sup> 40 wet	0.5	2	95	72	12	11
10	Pt <sup>(0)</sup> EnCat <sup>TM</sup> 40 dry	5	0.5	100	87	13	0
11	Pt <sup>(0)</sup> EnCat <sup>TM</sup> 40 dry	1	2	100	90	10	0
12	Pt <sup>(0)</sup> EnCat <sup>TM</sup> 40 dry	0.5	2	100	86	13	1

<sup>[a]</sup> Experimental conditions: 2 mol substrat in 20 mL MeOH solvent (HPLC grade), under hydrogen balloon room temperature conditions. 1% Pt/C; 5% Pt/SiO<sub>2</sub>, granules; Reaxa Pt<sup>(0)</sup>EnCat<sup>TM</sup>40, 0.112 mmol g<sup>-1</sup> Pt, 40% humidity, were bought from Aldrich.

<sup>[b]</sup> Evaluated by GC/MS analysis.

secondary products beyond aniline are observed only with 0.5 mol% catalytic amount (entry 12), pointing to the detrimental effect of adsorbed water on the chemoselectivity. In all reactions (entries 1–9) indeed secondary products beyond aniline were observed by GC/MS, confirming the moderate overall selectivity of supported Pt catalysts lamented by Corma and co-workers.<sup>[5]</sup>

In comparison to other Pt(0) heterogeneous catalysts [Pt(0)/C, Pt(0)/SiO<sub>2</sub>, Reaxa Pt<sup>0</sup>EnCat<sup>TM</sup>40], hence, the SiliaCat Pt<sup>0</sup>-2 catalyst proved to be much more reactive affording complete conversion after 0.5 h with 0.5 mol% amount only. Furthermore, selectivity (entry 6 in Table 3) was definitely higher with

only 4% aniline formed as by-product and no secondary products observed in solution. As a further element of comparison, lower values for the chemoselective hydrogenation of nitroarenes with carbon nanofiber-supported Pt nanoparticles required the employment of 3–10 atm H<sub>2</sub> and a temperature up to 50 °C.<sup>[8]</sup>

### Catalyst Selectivity

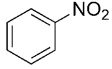
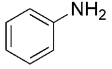
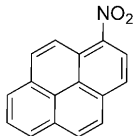
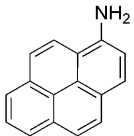
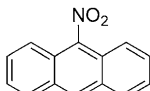
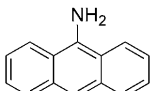
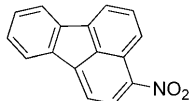
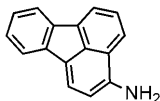
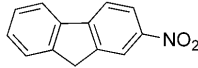
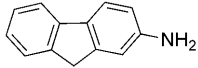
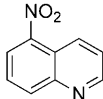
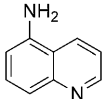
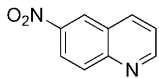
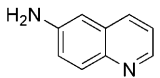
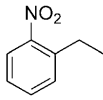
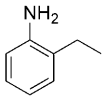
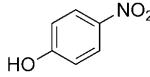
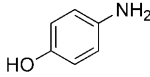
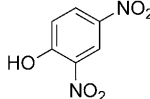
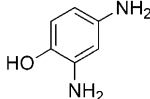
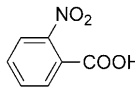
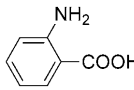
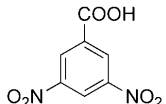
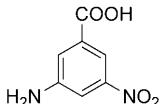
Hydrogenation of different nitro compounds as well as of different nitro compounds containing different functionalities was attempted in order to explore the selectivity of SiliaCat Pt<sup>0</sup>-2 catalyst in a wide range of

reactions. The material was tested under hydrogen balloon, room temperature conditions in methanol solvent with 0.5–1 mol% ORMOSIL-entrapped Pt catalyst (ORMOSIL, or organically modified silicate). The results in Table 5 show that in general complete substrate conversion was obtained after 0.5–4 h, typically after 1 h.

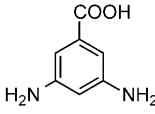
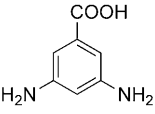
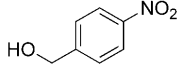
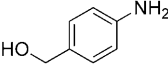
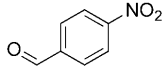
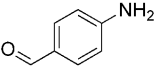
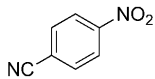
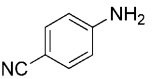
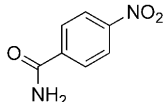
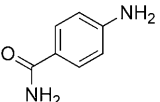
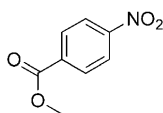
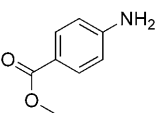
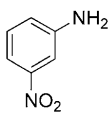
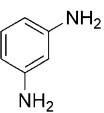
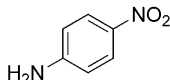
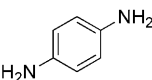
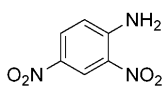
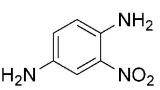
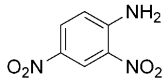
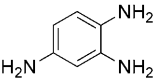
Entries 1–5 in Table 5 show that nitroarenes of widely different molecular size are selectively and en-

tirely converted into the nitroanilines under remarkably mild conditions. Entries 14–22 similarly show that the nitro group can be selectively reduced under the same mild conditions when other reducible groups such as carbonyl, amide, and esters are present. Only the nitrile group is not compatible with the SiliaCat Pt<sup>0</sup>-2 catalyst. Hence, for example, the –CN group is cleaved in the conversion of *p*-nitrobenzonitrile

**Table 5.** Selective catalytic hydrogenation with SiliaCat Pt<sup>0</sup>-2 under mild conditions of different nitro compounds and of different nitro compounds containing different functionalities.<sup>[a]</sup>

Entry	Substrates	Catalyst <sup>[b]</sup> (mol%)	Solvent <sup>[c]</sup> (M)	Time [h]	Product	Conv. (Yield) <sup>[d]</sup> [%]	Select. <sup>[d]</sup> [%]
1		0.5	MeOH (0.1 M)	1		100	100
2		0.5	MeOH (0.05 M)	1		100	98 <sup>[e]</sup>
3		1	MeOH (0.05 M)	4		100	85 <sup>[f]</sup>
4		0.5	MeOH (0.05 M)	1		100 (99.3)	100
5		0.5	MeOH (0.05 M)	1		98	100
6		1	MeOH (0.1 M)	0.5		100	98 <sup>[g]</sup>
7		1	MeOH (0.07 M)	1		100	96 <sup>[g]</sup>
8		0.5	MeOH (0.1 M)	1		100 (99.6)	100
9		1	MeOH (0.1 M)	1		100	100
10		1	MeOH (0.1 M)	1		100	98
11		0.5	MeOH (0.1 M)	1		100	100
12		0.5	MeOH (0.1 M)	2		100	98 <sup>[h]</sup>

**Table 5.** (Continued)

Entry	Substrates	Catalyst <sup>[b]</sup> (mol%)	Solvent <sup>[c]</sup> (M)	Time [h]	Product	Conv. (Yield) <sup>[d]</sup> [%]	Select. <sup>[d]</sup> [%]
13		1	MeOH (0.1 M)	2		100	100 <sup>[h]</sup>
14		0.5	MeOH (0.1 M)	1		100	100
15		0.5	MeOH (0.1 M)	1		100	95
16		1	MeOH (0.1 M)	0.5		92	13
17		0.5	MeOH (0.07 M)	2		100	80
18		0.5	MeOH (0.1 M)	0.5		100 (99.7)	100
19		1	MeOH (0.1 M)	1		100	100
20		0.5	MeOH (0.1 M)	2		100 (99.5)	100
21		0.5	MeOH (0.07 M)	0.5		100	95 <sup>[i]</sup>
22		0.5	MeOH (0.07 M)	1		100 (99)	100 <sup>[j]</sup>

<sup>[a]</sup> *Experimental conditions:* the substrate, 0.5–1 mol% Pt with respect to the substrate and the MeOH solvent (0.1 M, molar concentration with respect to the substrate) were stirred under hydrogen balloon/room temperature conditions.

<sup>[b]</sup> Catalyst identified in Table 1.

<sup>[c]</sup> Molar concentration of the solvent with respect to the substrate.

<sup>[d]</sup> Conversion and selectivity with respect to desired product were evaluated by GC/MS analysis. Isolated yield in crude product.

<sup>[e]</sup> 2% pyrene

<sup>[f]</sup> 15% anthracene.

<sup>[g]</sup> 2% or 4% quinoline.

<sup>[h]</sup> If 0.5 mol% SiliaCat Pt<sup>0</sup> catalyst was used, 98% of the –NO<sub>2</sub> group was reduced. If 1 mol% SiliaCat Pt<sup>0</sup> catalyst was used, both nitro groups were reduced.

<sup>[i]</sup> After 0.5 h one nitro group was reduced and 1,2-diamino-4-nitrobenzene was formed in 5% yield. After 1 h both nitro groups were reduced.

(entry 16) affording aniline as main reaction product, with only 13% of the desired *p*-cyanoaniline.

In each case, the hydrogenation reaction takes place consecutively. Hence, the regioselective hydrogenation of a specific nitro group in a polynitroarene is possible by simply controlling the reaction time.

Entries 21 and 22 in Table 5 show that in the reduction of 2,4-dinitroaniline one nitro group is reduced after 0.5 h, with 1,2-diamino-4-nitrobenzene being present in a 5% amount. After 1 h, however, both nitro groups were reduced affording 2,4-diaminobenzylamine. Hence, SiliaCat Pt<sup>0</sup>-2 solves a major problem en-

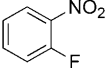
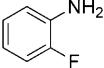
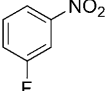
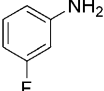
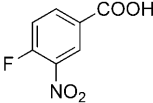
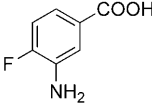
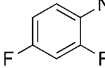
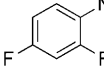
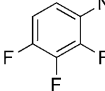
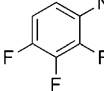
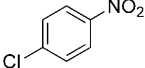
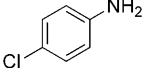
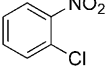
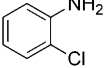
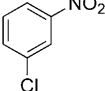
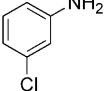
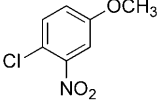
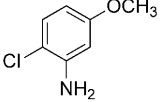
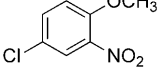
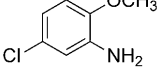
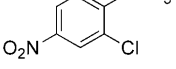
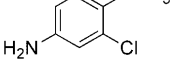
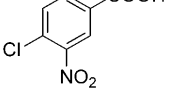
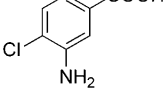
countered with the preparation of nitroanilines from dinitroarenes that in most cases requires stoichiometric sulfide reduction.<sup>[9]</sup>

Different nitro compounds containing different halides functionalities (F, Cl, Br, I) were also tested. SiliaCat Pt<sup>0</sup>-2 was tested in the selective catalytic hydrogenation of different halide aromatic nitro compounds under hydrogen balloon/room temperature conditions. The reactions had been studied in methanol solvent with 0.5–1 mol% silica gel supported platinum catalyst.

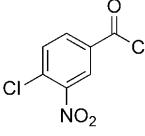
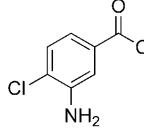
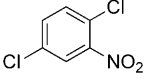
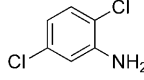
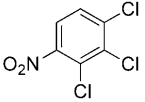
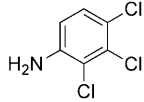
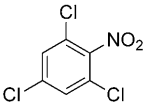
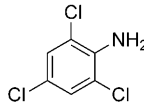
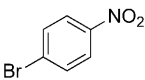
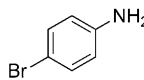
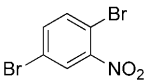
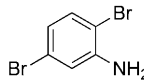
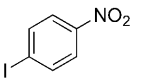
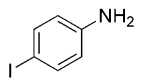
Complete conversion was obtained after 0.5–2 h, typically after 1 h (Table 6).

The results in Table 6 show that -NO<sub>2</sub> groups in nitroarenes can be selectively reduced under mild conditions also when different halides are present in the same molecule. Hence, when an F substituent is present the nitro group in the nitroarene was reduced with >99% selectivity (entries 1–5 in Table 6). If a Cl substituent is present the nitro group is reduced at somewhat lower >80% selectivity (entries 6–16). The chemoselective hydrogenation of nitroarenes with Br

**Table 6.** Selective hydrogenation of aromatic nitro compounds in the presence of different halides using SiliaCat Pt<sup>0</sup>-2 catalyst.

Entry	Substrate	Catalyst (mol%)	Solvent <sup>[a]</sup> (M)	Time [h]	Product	Conv. (Yield) <sup>[b]</sup> [%]	Select. <sup>[b]</sup> [%]
1		0.5	MeOH (0.1 M)	1		100 (99.1)	100
2		0.5	MeOH (0.1 M)	0.5		100	100
3		0.5	MeOH (0.1 M)	1		100	99
4		0.5	MeOH (0.1 M)	1		100 (99.4)	100
5		0.5	MeOH (0.1 M)	1		100 (99.3)	100
6		0.5	MeOH (0.1 M)	0.5		100	87
7		0.5	MeOH (0.1 M)	1		100	93
8		0.5	MeOH (0.1 M)	1		100	85
9		1	MeOH (0.1 M)	0.5		100	93
10		1	MeOH (0.1 M)	0.75		100	98
11		1	MeOH (0.1 M)	0.5		100	91
12		1	MeOH (0.1 M)	1		96	87

**Table 6.** (Continued)

Entry	Substrate	Catalyst (mol%)	Solvent <sup>[a]</sup> (M)	Time [h]	Product	Conv. (Yield) <sup>[b]</sup> [%]	Select. <sup>[b]</sup> [%]
13		1	MeOH (0.1 M)	2		90	80
14		0.5	MeOH (0.1 M)	1		100	87 <sup>[c]</sup>
15		0.5	MeOH (0.1 M)	1		100 (99.3)	91 <sup>[d]</sup>
16		0.5	MeOH (0.1 M)	1		99	87 <sup>[d]</sup>
17		0.5	MeOH (0.07 M)	1		100	85
18		0.5	MeOH (0.1 M)	1		100	80 <sup>[e]</sup>
19		0.5	MeOH (0.05 M)	2		51	50

<sup>[a]</sup> Molar concentration of the solvent with respect to the substrate.

<sup>[b]</sup> Conversion and selectivity to desired product by GC/MS analysis. Isolated yield in crude product.

<sup>[c]</sup> 13% of chloroaniline product was obtained.

<sup>[d]</sup> The dichloroaniline product was obtained.

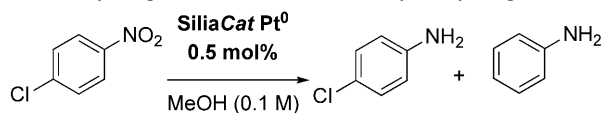
<sup>[e]</sup> 20% of bromoaniline product was obtained.

and I substituents, known to be much more demanding than for chloronitroarenes using traditional catalysts,<sup>[4]</sup> is now achieved with >80% selectivity in the case of Br (entries 17 and 18). Only in the case of I was the conversion reduced to 51% with only 50% selectivity (entry 19). These results are remarkable also from a fundamental mechanistic viewpoint because as a general rule accumulation of ArNHOH is favored at low temperature (as intermediates are often unstable at high temperature) and when electron-withdrawing substituents are present.

### Catalyst Leaching and Reusability

The reusability test of the catalyst *SiliaCat Pt<sup>0</sup>-2* was studied using 4-chloronitrobenzene as substrate under the optimal reaction conditions identified above. Reusing the catalyst in 7 consecutive cycles (Table 7) did not result in any loss in catalytic activity with minimal leaching of Pt and Si (assessed by ICP-MS). Complete substrate conversion was obtained even after the seventh cycle, with 99% selectivity.

The selectivity of the reaction even improves with every single recycle going from 84% up to 99% in run 7. No exfoliation of the catalyst takes place (as evidenced by the leaching test described in the Experimental Section); whereas no changes in the size and nature of the Pt crystallite size has been observed by XRD analysis prior to and after the 7 reaction cycles. The positive-feedback phenomenon of affective selectivity in consecutive reaction cycles has already been observed by some of us with catalytic ORMOSIL doped with TEMPO in the biphasic selective oxidation of alcohols to carbonyl compounds with NaOCl.<sup>[10]</sup> Such as in the latter case, we ascribe this phenomenon to the matrix alkylation typical of ORMOSIL materials that markedly differentiates the behaviour of these materials from that of analogous silica-supported materials. A *cooperative* mechanism may be in action through which the more substrate (and product) molecules are adsorbed (and formed) within the inner sol-gel cage surface, the faster is the diffusion of the reactant and product molecules through the porous network. Notably, an analogous explanation was recently proposed to explain the re-

**Table 7.** Reusability of the SiliaCat Pt<sup>0</sup>-2 Hydrogel in the selective catalytic hydrogenation of 4-chloro-nitrobenzene.

Entry	Time [h]	Conversion (Yield) <sup>[a]</sup> [%]		Leaching <sup>[b]</sup> [ppm]	
		4-Chloroaniline	Aniline	Pt	Si
Run 1	0.5	84	12	0.2 (0.69)	1.2 (4.2)
Run 2	0.5	89	11	0.04 (0.15)	0.4 (1.2)
Run 3	0.5	90	10	0.02 (0.4)	0.08 (0.4)
Run 4	0.5	92	8	0.17 (1.05)	0.1 (0.5)
Run 5	0.5	98	2	0.01 (0.1)	0.1 (0.5)
Run 6	0.5	99 (98.2)	1	0.01 (0.1)	0.12 (0.6)
Run 7	0.5	99 (98.5)	1	0.01 (0.1)	0.08 (0.4)

<sup>[a]</sup> Amount in final product determined by GS/MS analysis. Isolated yield of the crude product.

<sup>[b]</sup> Leaching in Pt and Si determined by ICP analysis in solution (DMF solvent 0.7 M, with respect to the crude product) and in the solid crude product.

sults of the adsorption properties of similar sol-gel doped ORMOSILs,<sup>[11]</sup> and was based on the observation that these materials are chemical *sponges* with chromatographic properties, i.e., they adsorb and concentrate the reagents at the cage surfaces where reactions take place, while the adsorbed molecules promote further diffusion of incoming reactants.

## Conclusions

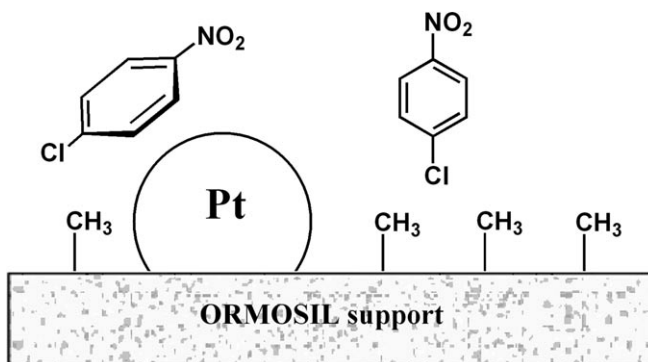
The hydrogenation of different nitro compounds and the selective hydrogenation of different nitro compounds in the presence of different functionalities including reducible carbonyl, amide, ester, amine and halide groups was achieved over SiliaCat Pt<sup>0</sup>-2 catalyst in methanol solvent at room temperature and at 1 bar H<sub>2</sub> pressure. The catalyst consists of a new nano-hybrid sol-gel ORMOSIL matrix entrapping nano-sized Pt(0) particles within the inner porosity of the organosilica matrix.

In agreement with similar recent findings describing a significant increase in selectivity for the hydrogenation of 3-nitrostyrene with decreasing metal crystallites size for Pt on carbon or TiO<sub>2</sub> supports,<sup>[12]</sup> we also observe an optimal particle size for our catalysts supported on methylsilica with well defined particle sizes (2.9 nm) which must be related to electronic effects responsible for a change in chemoselectivity. When metal nanoparticles are present, the nitro group is selectively adsorbed to the metal surface where hydrogenation takes place, whereas interaction with other substituents of the nitroarene (taking place in large metal particles and flat surfaces) is minimized.

The sol-gel entrapment of the Pt isolated metallic nanophase within the ORMOSIL structure ensures

three concomitant advantages. On one side, the strongly lipophilic nature of the ORMOSIL matrix ensures preferential adsorption of the less reactive (lipophilic) moiety of the substrate dictating preferential access of the most reactive NO<sub>2</sub> groups to the hydride groups adsorbed on the Pt nanoparticles (Figure 1).<sup>[13]</sup>

On the other hand, the well known hydrophobic nature of fully alkyl-modified silica xerogels ensures the absence of water from the material surface,<sup>[14]</sup> that instead leads to secondary by-products formation observed with the most common commercial supported Pt catalysts. Finally, the encapsulation within the sol-gel cages ensures physical and chemical stabilization of the isolated Pt ensembles,<sup>[15]</sup> and thus prolonged activity of the catalyst with a unique “positive feedback” effect that is typical of sol-gel doped ORMOSIL. Given the broad applicability of Pt-based catalysts to widely different chemical reactions, it is envis-



**Figure 1.** Schematic representation of adsorbed 4-chloro-nitrobenzene on a hydrogen saturated SiliaCat Pt<sup>0</sup>-Hydrogel catalyst.



aged that these catalysts, now commercially available, will find application in numerous fields of chemical synthesis as well as in energy generation.

## Experimental Section

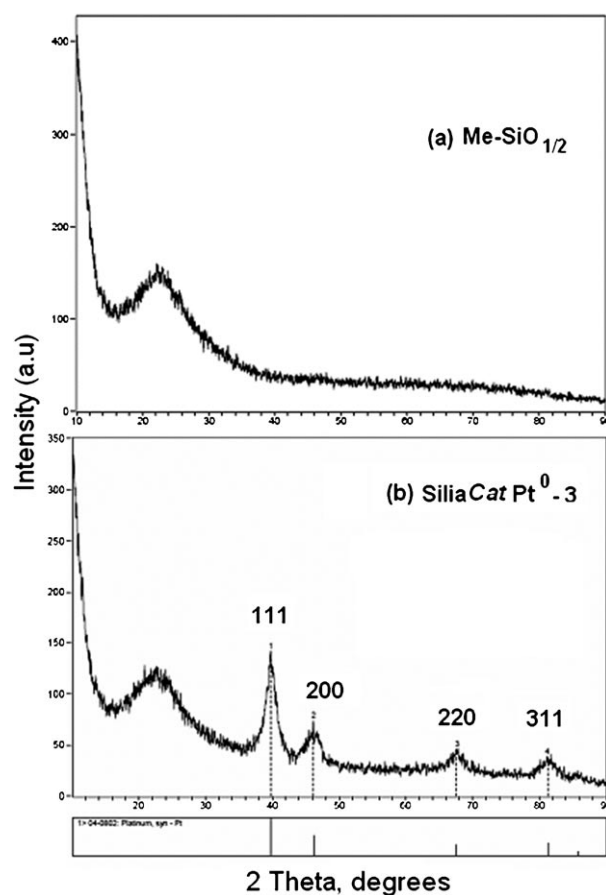
### Catalyst Preparation

A mixture of methyltriethoxysilane (27 g, 30 mL, 151.4 mmol) and 10 mL of 0.042 M  $\text{HCl}_{\text{aq}}$  (0.42 mmol  $\text{H}^+$  and 555 mmol  $\text{H}_2\text{O}$ ) was stirred vigorously for 15 min (or until the solution became homogeneous). The resulting solution was concentrated on a rotavapor at 30 °C under reduced pressure to remove almost all ethanol (about 15 min). To the alcohol-free sol thereby obtained was added  $\text{K}_2\text{PtCl}_4$  (from 0.004 to 0.018 equiv.) dissolved in  $\text{H}_2\text{O}$  (from 5 to 10 mL) and 60 mL acetonitrile. To the resulting mixture was added 1 M NaOH (from 0.023 to 0.053 equiv.) to favour gelation that indeed rapidly occurred. The resulting light-orange homogeneous and transparent gel was left to dry in air for 4 days. The dark-blue xerogel obtained was then reduced at room temperature with a solution of sodium borohydride in  $\text{THF}:\text{H}_2\text{O}=1:1$ , ( $\text{Pt}:\text{NaBH}_4=1:12$  molar ratio; 180 mL), washed with  $\text{H}_2\text{O}$  and THF and left open to dry at room temperature.

### Material Characterization

The SEM pictures (Figure 2) of *SiliaCat Pt<sup>0</sup>*-Hydrogel heterogeneous catalyst reveal the typical matrix structure of organosilica particles. The amorphous nature of the  $\text{MeSiO}_{1/2}$  physically doped material is confirmed by the characteristic wide diffractogram displayed in Figure 3, **a**.

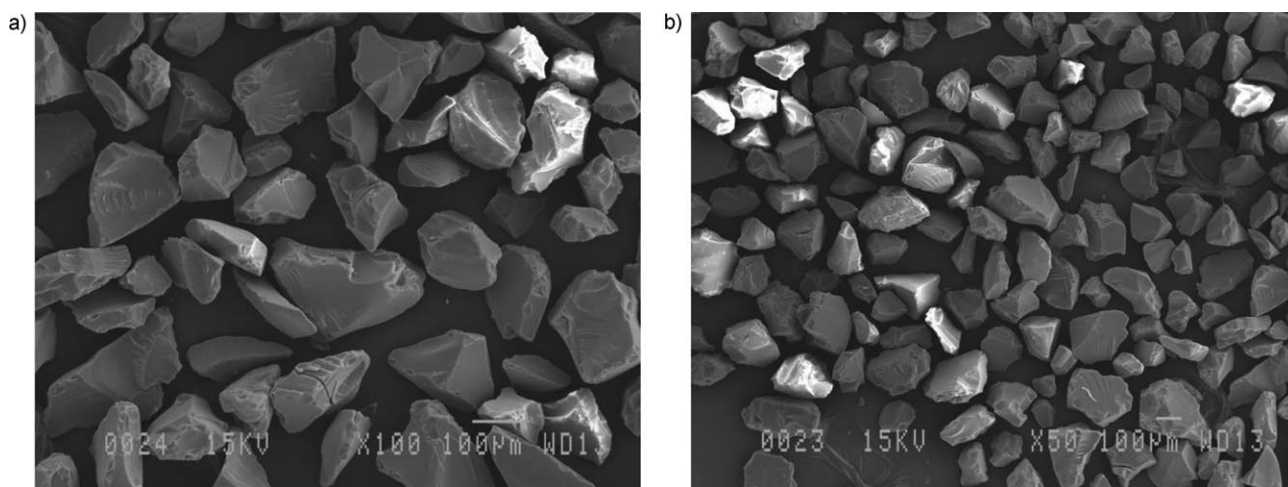
The dopant metallite particles, however, are made of nanostructured crystalline platinum(0). This is clearly shown by the X-ray diffraction (XRD) pattern of the powder in which the crystalline nature of the active nanophase is evident from the succession of peaks (Table 8, Figure 3, **b**) typical of the face-centered cubic structure of metallic Pt. A typical metallite particles size calculated for *SiliaCat Pt<sup>0</sup>* from



**Figure 3.** Powder X-ray diffraction (XRD) patterns of the amorphous  $\text{MeSiO}_{1/2}$  material (**a**) and of the *SiliaCat Pt<sup>0</sup>*-3 heterogeneous catalyst (**b**).

the line broadening of (111) reflection using the Scherrer formula is from 1.7 to 3.15 nm (Table 8).

Solid-state  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker Avance spectrometer (Milton, ON, Canada) at a silicon frequency of 79.5 MHz. Samples were spun at 8 kHz at magic

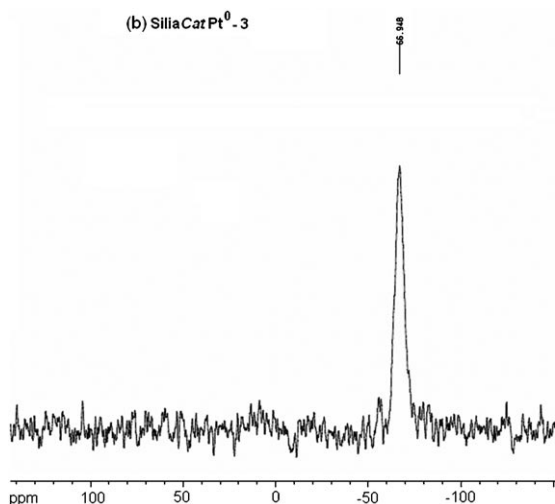


**Figure 2.** *SiliaCat Pt<sup>0</sup>*-1 – particle sizes: from 60 to 250  $\mu\text{m}$ .

**Table 8.** X-ray powder diffraction (XRD) of SiliaCat Pt<sup>0</sup>-3.

Catalyst	Diffraction angle 2θ				Mean particle size [nm]
	111	200	220	311	
Pt <sup>(0)</sup> <sup>[a]</sup>	39.76	46.24	67.46	51.29	N.A.
SiliaCat Pt <sup>0</sup> -1	39.76	46.16	67.74	81.12	1.7
SiliaCat Pt <sup>0</sup> -2	39.86	46.04	67.52	80.62	2.92
SiliaCat Pt <sup>0</sup> -3	39.76	46.16	67.62	81.25	3.15

<sup>[a]</sup> The Powder Diffraction File of the International Centre for Diffraction Data was used to identify the diffraction peaks characteristic of crystalline Pt(0) with a face-centered cubic (fcc) lattice.

**Figure 4.** <sup>29</sup>Si NMR spectra of SiliaCat Pt<sup>0</sup>-3 heterogeneous catalysts.

angle at room temperature in a 4 mm ZrO rotor. A Hahn echo sequence synchronized with the spinning speed was used while applying a TPPM15 composite pulse decoupling during acquisition. 2400 acquisitions were recorded with a recycling delay of 30 seconds. The catalyst analyzed (Figure 4 and Table 9) was SiliaCat Pt<sup>0</sup>-3.

Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micrometrics TriStar<sup>™</sup> 3000 system. The data were analyzed using the Tristar 3000 model 4.01. Both adsorption and desorption branches are used to calculate the pore size distribution. The metal content in the products was measured using the CAMECA SX100 instrument equipped with EPMA analyse technique, a fully qualitative and quantitative method of non-destructive elemental analysis of micron-sized volumes at the surface of materials, with a sensitivity at the level of ppm.

### Catalyst Activity and Reusability

Reactions were performed on a 2-mmol scale. The substrate was dissolved in 20 mL of MeOH and then treated with 0.1–1 mol% sol-gel entrapped catalyst. The mixture was degassed two times, replacing each time the vacuum by hydrogen. The reaction mixture, connected to a balloon of hydrogen, was stirred at room temperature until it showed maxi-

**Table 9.** <sup>29</sup>Si solid state NMR spectra of SiliaCat Pt<sup>0</sup>-3 catalyst.

Catalyst <sup>[a]</sup>	T <sub>1</sub> [ppm]	T <sub>2</sub> [ppm]	T <sub>3</sub> [ppm]	T <sub>1</sub> :T <sub>2</sub> :T <sub>3</sub> [%]
Ref. <sup>[16]</sup>	-46	-56.00	-66.00	
MeSiO <sub>1/2</sub> <sup>[b]</sup>	0	-55.58	-66.38	0:10:90
SiliaCat Pt <sup>0</sup> -3	0	-55.42	-66.94	0:5:95

<sup>[a]</sup> Catalyst identified in Table 1.

<sup>[b]</sup> Silica gel support without platinum, (blank from our measurements).

mum conversion. The catalyst was then filtered off and washed with EtOH or MeOH. The filtrate was concentrated to give a crude product and the conversion in the desired product was determined by GC/MS analysis.

In the reusability test the hydrogenation was carried out under a hydrogen balloon at room temperature in the presence of 0.5 mol% sol-gel catalyst. A two-necked flask connected to a balloon of hydrogen was charged with the SiliaCat Pt-2 catalyst and degassed twice replacing each time the vacuum with H<sub>2</sub>. The solution of the substrate in anhydrous methanol (0.1 M with respect to the substrate), kept under inert conditions, was transferred *via* cannula to a flask charged with the catalyst. The resulting mixture was degassed once more and the vacuum was replaced with H<sub>2</sub> followed by 30 min stirring after which the catalyst was recovered by filtration, rinsed with MeOH/THF solvents and dried under vacuum prior to reuse. The conversion was assessed by GC/MS analysis and the filtrate was concentrated to give a crude product that was analyzed by ICP-MS for leaching of Pt and Si.

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