Selective Hydrogenation of Vegetable Oils over SiliaCat Pd(0)

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ABSTRACT: Nanostructured immobilized-Pd catalyst SiliaCat Pd(0) selectively mediates at room temperature the selective and complete hydrogenation of a wide variety of vegetable oils under hydrogen balloon conditions over 0.1 mol % (based on metal content) entrapped catalyst. No *cis/trans* isomerisation takes place, whereas the catalyst is truly recyclable with low leached amounts of valued palladium, thereby providing the fat and oleochemicals industry with a suitable replacement for Ni-based catalysts.

1. INTRODUCTION

Hardening of unsaturated fatty acids (FA) or fatty acid methyl esters (FAME) through catalytic hydrogenation is a fundamental industrial reaction carried out worldwide on very large scale since the early 1900s to manufacture basic oleochemicals, such as stabilizers and surfactants, and edible fats, such as margarine.[1] Average annual world oil production in the years 1996−2000 amounted to 105×10^6 t and is expected to increase to 185×10^6 t in the years 2016−2020, with about 80% of the global oil and fat production being made of vegetable oils.[2]

From the beginning, the hydrogenation of FA or FAME has been heterogeneously catalyzed with Ni in suspension (today over Ni finely divided and supported on alumina or kieselguhr),[3] mostly in a batch process in a reactor under relatively high H_2 pressure (15−20 bar) and elevated temperature (180−230 °C) followed by the removal of the catalyst by time-consuming filtration with frequent Ni-soaps formation. Under these conditions nickel can indeed react with components of the fat to form fat-soluble salts which may contaminate the product,[4] while a significant degree of *cis/trans* isomerization leads to formation of unhealthy *trans* fatty acid chains.

To improve the hardening process and eliminate these disadvantages either fixed bed methods using Ni-based catalysts have been developed[5] or replacement of nickel with palladium has been investigated (since the early 1960s).[6] Research nowadays continues in the context of biomass valorization through hydrogenation.[7] Yet, results of pure margarines production over Pd catalysts thus far have been uneconomical, as the amount of costly palladium employed needs to be significantly reduced and the catalyst recycled.[8] Furthermore, because the specification limit for the residual Pd in food is 10-fold lower than that of micronutrient Ni (100 vs 1,000 μg/day oral tolerable daily intake upper limit, respectively),[9] the amount of Pd catalyst leached should be minimized; otherwise, Ni will continue to be used even though Ni in general shows lower activity than Pd.

In this context, we recently reported that a newly developed series of commercial sol−gel entrapped Pd catalyst trade named SiliaCat Pd(0) made of ultrasmall Pd nanoparticles (4−6 nm large) encapsulated within an organosilica matrix is a good mediator for the selective hydrogenation of nitroarenes.[10] Now we report the discovery that SiliaCat Pd(0) is a chemoselective and efficient heterogeneous catalysts for the leach-proof hydrogenation of a wide variety of vegetable oils in a simple hydrogen balloon at room temperature. An ultralow amount of catalyst (0.1 mol %) is enough to promote full hydrogenation of FA, FAME, and vegetable oils with no isomerization and with negligible leaching of valued Pd. The catalyst is fully reusable, opening the route to replacement of Ni catalyst in the fat and oleochemicals industry.

2. EXPERIMENTAL SECTION

The catalyst preparation has been described in detail elsewhere.[11] Herein a 0.1−1 mol % SiliaCat Pd(0) sol−gel entrapped catalyst amount was employed (0.05 mmol g^{-1} Pd load from CAMECA SX100 equipped with an EPMA microanalyzer). Reactions were performed on a 3, 4, 5, or 6 mmol substrate scale dissolved in 20 mL of HPLC grade solvent for 0.15 M, 0.2 M, 0.25 M, or 0.3 M concentration, or on a 14.5 mmol substrate scale dissolved in 30 mL of THF or a THF/MeOH mixture (5:1 by volume ratio) for 0.5 M concentration.

The mixture was degassed two times, replacing each time the vacuum by hydrogen. The reaction mixture connected to a hydrogen balloon was vigorously stirred at room temperature until it showed maximum conversion. The isolated yields are not given because during isolation of the product we lose a small amount of the product. THF (50 mL) was then added and the catalyst filtered and rinsed with extra THF, or the reaction mixture was heated at 40 °C and the catalyst filtered and rinsed with THF. The filtrate was concentrated to give a crude product that was each time analyzed by ICP-OES for leaching of Pd and Si.

In the reusability test the hydrogenation was carried out in a hydrogen balloon at room temperature in the presence of the same sol−gel catalyst. A two-necked flask connected to a balloon of hydrogen was charged with the substrate, the solvent, and SiliaCat Pd(0) catalyst in 0.1 mol % amount. The mixture was degassed two times, replacing each time the

vacuum by hydrogen. The reaction mixture connected to the balloon of hydrogen was vigorously stirred at room temperature for 3 h, after which THF (50 mL) was added and the catalyst recovered by filtration, rinsed with THF, and dried under vacuum prior to reuse. The filtrate was concentrated to give a crude product that was analyzed by ICP-OES for leaching of Pd and Si. Conversion was assessed by TLC analysis (hexane/ethyl acetate = 5:1) using potassium permanganate stain, by GC/MS analysis, and by ^{1}H NMR of isolated crude product.

3. RESULTS AND DISCUSSION

3.1. Solvent Effect. To study the influence of the solvent on the catalytic process, a Silia*Cat* Pd(0) catalyst sample (0.05 mmol g^{-1} Pd load) was first tested in hydrogenation of oleic acid (*cis* C18:1, **1** (Figure 1) in methanol, ethanol, tetrahydrofuran, hexane, and ethyl acetate (Table 1).
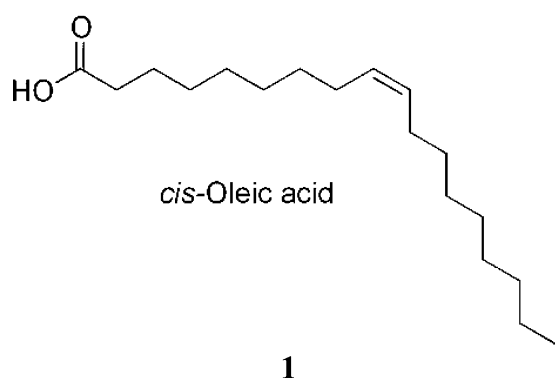

Figure 1.

The best results were obtained in methanol (0.25 M concentration with respect to the substrate) and in THF/MeOH 5:1 by volume ratio (0.5 M concentration with respect to the substrate) over 0.1 mol % catalyst (entries 3 and 11 in Table 1). The hydrogenation reaction involved directly total saturation of *cis* C18:1 to C18:0. No isomerization reaction of *cis* C18:1 to *trans* C18:1 was observed.

3.2. Scope of the Method. To evaluate the catalyst activity, the same substrate was hydrogenated with different amounts of catalyst in the optimal solvent system (THF/MeOH, 5:1 by volume ratio) and in MeOH 0.25 M under the mild conditions of Table 1. Results in Table 2 show that, after 30 min of hydrogenation over 0.5−1 mol %, Pd proceeds with full oleic acid conversion (entries 1, 3, and 4) whereas the reaction time extends to 2−3 h over 0.1 mol % Pd depending on the solvent (entries 2 and 6).

To further investigate the catalyst selectivity, hydrogenation of different fatty acids containing different numbers of double bonds was attempted. Reactions were conducted in methanol 0.25 M under the conditions of Table 1 over 0.1−0.2 mol % Silia*Cat* Pd(0).

The results in Table 3 show that complete substrate conversion into the corresponding saturated product was obtained after 3−5 h. For instance (entry 1), in 3 h oleic acid (*cis* C18:1) was completely converted to stearic acid (*cis* C18:0) with no *cis* to *trans* isomerization reaction also in methanol. Hydrogenation of linoleic acid (*cis* C18:2, **2** (Figure 2)) involved consecutive saturation steps: first, after 1 h, to *cis* C18:1 in 90% yield, followed by subsequent saturation of *cis* C18:1 to *cis* C18:0 after 3 more hours (entry 2 in Table 3).

Hydrogenation of linolenic acid (*cis* C18:3, **3** (Figure 3)) involved consecutive saturation to *cis* C18:1 in 100% conversion after 2 h and subsequent saturation of *cis* C18:1 to *cis* C18:0 after 3 more hours (entry 3).

Also the hydrogenation of eicosapentaenoic acid ethyl esther (EPA, *cis* C20:5, **4** (Figure 4)) resulted in complete saturation to *cis* C20:0 with 100% conversion after 3 h; similarly to the hydrogenation of erucic acid (*cis* C22:1, **5** (Figure 5)), affording complete saturation to *cis* C22:0 after 3 h. Again, isomerization reactions of *cis* to *trans* isomers were not observed.

To explore the scope of the method, different vegetable oils were then hydrogenated under the same optimized reaction conditions of Table 1 in THF/MeOH (0.5 M) over 0.1 mol % Silia*Cat* Pd(0). The results in Table 4 show that, in general, complete substrate conversion of the vegetable oil to saturated product was obtained after 3 h.

3.3. Leaching and Catalyst Reusability. Leaching of Pd from the catalyst was in each case tested by ICP-OES in the reaction products. Solid Pd catalysts are notorious leachers[12], and we have recently investigated the leaching issue in heterogeneous Pd catalysis.[13] Here, catalysis was truly heterogeneous, as shown by lack of reactivity of the reaction filtrate obtained after 20 min of oleic acid conversion under the optimized reaction conditions of Table 1. In general, the last columns in Tables 1, 3, and 4 show that varying the reaction conditions in the hydrogenation of oleic acid (Table 1) or the FA (Table 3) or vegetable oil (Table 4) substrates resulted in values of leached Pd in the isolated crude product that are <1 ppm.

The structure of the sol−gel nanocatalysts leads to such low leaching of precious metal that the use of an ultralow amount of catalyst (0.1 mol %) in an hydrogen balloon is enabled. Both the latter factors indeed are known[14] to ensure stabilisation of the metal in its metallic or hydridic form, through higher availability of H$_2$ at the catalytically active Pd^0 particles, thus sustaining the catalytic activity of the entrapped palladium.

Accordingly, the reusability of the catalyst studied using linolenic acid (C18:3) as substrate in five consecutive cycles under the reaction conditions identified in Table 4 shows (Table 5) full retention of the catalytic activity with minimal leaching of Pd and Si. Complete substrate conversion in saturated product (C18:0) with 96% selectivity was obtained even after the fifth cycle.

The isolated yields in the entries 1 and 2 of Table 5 are lower than the total conversion observed by GC/MS because during isolation of the product a small amount of product is inevitably lost. In entries 3 and 4 total conversion of the substrate is observed, but a 1−3% of oleic acid nonselectively forms. Similarly, in entry 5 the conversion of the substrate is 99% but the yield by GC (MS) of final product is 95% (5% oleic acid), so that the overall selectivity as defined in Table 5 is only 96%.

In conclusion, we have discovered that a modest 0.1 mol % amount of Silia*Cat* Pd(0) selectively mediates the full conversion of saturated vegetable oils at room temperature under hydrogen balloon conditions. The catalyst is reusable with negligible leaching of valued palladium. For comparison, at the end of the 1990s, a state of the art 0.005% (wt %) Pd/Al$_2$O$_3$ catalyst for vegetable oils hydrogenation required a reaction temperature of 102 °C in a continuous process,[15] whereas a more recent catalyst made of Pd nanoparticles entrapped in the hexagonal porosity of SBA-15 mesoporous silica afforded similar good results at 100 °C under 5 atm H$_2$.[16]

Table 1. Influence of the Solvent on the Catalytic Activity of Silia*Cat* Pd(0) Heterogeneous Catalyst in the Hydrogenation Reaction of Oleic Acid[a]

entry	catalyst (mol %)	solvent (M)[c]	time (h)	conv[d] (%)	yield[d] (%)	leaching (ppm)[e] Pd	Si
1	0.1	MeOH (0.15 M)	1	62	99.6	0.62 (12.2)	0.09 (1.9)
			4	100			
2	0.1	MeOH (0.2 M)	1	65	98.9	0.5 (10.1)	0.11 (2.2)
			3	100			
3	0.1	MeOH (0.25 M)	3	100	99.5	0.2 (4.81)	0.10 (2.0)
4	0.1	MeOH (0.3 M)	1	51	99.8	0.49 (9.8)	0.12 (2.4)
			4	100			
5	0.1	THF (0.25 M)	4	25			
6	0.2	THF (0.25 M)	4	72	99.5		
			6	100			
7	0.5	THF (0.25 M)	2	84	98.1	0.65 (13.0)	0.13 (2.6)
			4	100			
8	0.1	THF (0.5 M)	4	76	99.3	0.28 (5.5)	0.15 (2.9)
			6	100			
9	0.2	THF (0.5 M)	2	88			
			4	100			
10	0.5	THF (0.5 M)	2	100	99		
11	0.1	THF/MeOH[b] (0.5 M)	2	100	98	0.32 (6.2)	0.19 (3.7)
12	0.5	EtOH (0.25 M)	1	80		0.45 (9.1)	0.13 (2.6)
			2	100			
13	0.5	ethyl acetate (0.25 M)	1	100		0.26 (4.5)	0.11 (2.3)

[a]*Experimental conditions*: 3 mmol substrate in 20 mL of HPLC grade solvent (0.15 M, entry 1), 4 mmol substrate in 20 mL of HPLC grade solvent (0.2 M, entry 2), 5 mmol substrate in 20 mL of HPLC grade solvent (0.25 M, entries 3, 5, 6, 7, 12, and 13), 6 mmol substrate in 20 mL of HPLC grade solvent (0.3 M, entry 4), 14.5 mmol substrate in 30 mL of HPLC grade solvent (0.5 M, entries 8–10), and 0.1–0.5 mol % Silia*Cat* Pd(0) catalyst under hydrogen balloon room temperature conditions. [b]14.5 mmol substrate in 30 mL of HPLC grade solvent (5:1 by volume ratio). [c]Molar concentration with respect to the substrate. [d]Conversion in final product evaluated by GC/MS analysis and ^{1}H NMR (isolated yield). [e]Leaching in Pd and Si determined by ICP-OES analysis in 1-pentanol solution (50 mg/mL) and in solid crude product.

Table 2. Catalytic Reactivity of Silia*Cat* Pd(0) Heterogeneous Catalyst in Hydrogenation of Oleic Acid[a]

entry	substrate	catalyst (mol %)	solvent (M)[c]	time (h)	conv (yield)[d] (%)	TON[e]	TOF[e] (h[−1])
1	oleic acid	0.5	MeOH/THF[b] (0.5 M)	0.5	100 (99.1)	200	400
2	oleic acid	0.1	MeOH/THF[b] (0.5 M)	2	100 (99.4)	1000	500
3	oleic acid	1	MeOH (0.25 M)	0.5	100 (99.3)	100	200
4	oleic acid	0.5	MeOH (0.25 M)	0.5	100 (99)	200	400
5	oleic acid	0.2	MeOH (0.25 M)	1	90	500	250
				2	100		
6	oleic acid	0.1	MeOH (0.25 M)	3	100 (99.5)	100	333

[a]5 mmol substrate in 20 mL of MeOH HPLC grade solvent and 0.1–1 mol % Silia*Cat* Pd(0) catalyst under hydrogen balloon room temperature conditions. [b]14.5 mmol substrate in 30 mL of THF/MeOH (5:1 v/v). [c]Molar concentration with respect to the substrate. [d]Evaluated by GC/MS analysis and ^{1}H NMR (isolated yield) [e]TON: mol of substrate converted per mol of Pd catalyst used in reaction. TOF = TON/h. For a total conversion of the substrate in the saturated product, TON is calculated as the amount of substrate (mmol) converted per the amount of Pd catalyst (mmol) used. TOF = TON/h.

Table 3. Catalytic Reduction with Silia*Cat* Pd(0) under Mild Conditions of Different Fatty Acids[a]

entry	substrate	catalyst (mol %)	reaction time (h)	conv (yield)[b] (%)	leaching[c] (ppm) Pd	Si
1	oleic acid (*cis* C18:1)	0.1	3	100 (99.5)	0.25 (4.8)	0.10 (2.0)
2	linoleic acid (*cis* C18:2)	0.1	4	100 (97.5)	0.25 (4.9)	0.19 (3.8)
3	α-linolenic acid (*cis* C18:3)	0.1	5	100 (99.4)	0.29 (5.7)	0.07 (1.4)
4[d]	eicosapentaenoic acid ethyl esther (*cis* C20:5)	0.2	3	100	0.13 (3.8)	0.18 (5.3)
5[d]	erucic acid (*cis* C22:1)	0.2	3	100		

[a]*Experimental conditions*: HPLC grade MeOH solvent (0.25 M with respect to the substrate) under hydrogen balloon room temperature conditions. [b]Conversion evaluated by GC/MS analysis (isolated yield). [c]Leaching of Pd and Si determined by ICP-OES analysis in 1-pentanol solution (50 mg/mL) and in solid crude product. [d]Eicosapentaenoic acid ethyl esther (*cis* C20:5) from Aldrich in 68.6% purity and erucic acid (*cis* C22:1) from Aldrich in 89.3% purity.
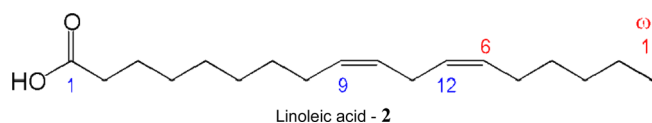
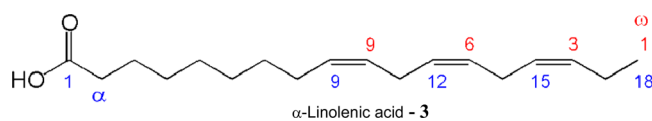Linoleic acid - **2**

Figure 2.

α-Linolenic acid - **3**

Figure 3.

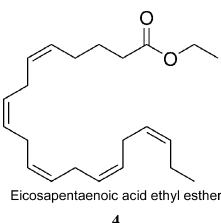Eicosapentaenoic acid ethyl esther
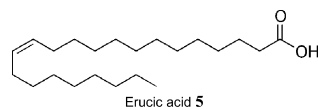**4**

Figure 4.

Erucic acid **5**

Figure 5.

Pd heterogenized on mesostructured SFA silica affords considerably lower *cis/trans* isomerization and milder reaction conditions due to the entirely different structure of the new heterogeneous organosilica catalyst that was recently described in detail.[17] First, the ∼3 nm Pd nanoparticles in Silia*Cat* Pd(0) are much smaller, which is known to enhance selective activity in hydrogenation reactions in general;[18] second, and more importantly, the organosilica sol−gel cages of Silia*Cat* Pd(0), opposed to the hydrohilipic mesopores of SBA-15, crucially dictate preferential access of the hydrophobic moiety of the vegetable oil to the entrapped Pd crystallites where molecular hydrogenation takes place.

Table 5. Reusability of the Silia*Cat* Pd(0) in the Catalytic Hydrogenation of Linolenic Acid (*cis* C18:3) under Mild Conditions[a]

entry	time (h)	conversion (yield)[b] (%)	selectivity[b] (%)	leaching (ppm)[c]	
				Pd	Si
1	3	100 (99.3)	100	0.08 (1.59)	0.19 (3.94)
2	3	100 (99.5)	100	0.16 (3.20)	0.15 (2.92)
3	3	100	99	0.22 (4.31)	0.23 (4.51)
4	3	100	97		
5	3	99	96		

[a]*Experimental conditions:* HPLC grade MeOH solvent (0.25 M with respect to the substrate) under hydrogen balloon room temperature conditions over 0.1 mol % Silia*Cat* Pd(0) catalyst (0.05 mmol/g palladium) under hydrogen balloon room temperature conditions. [b]Conversion and selectivity to desired product determined by GC/MS analysis (selectivity = yield by GC/MS/total conversion × 100). Isolated yield of the crude product. [c]Leaching in Pd and Si determined by ICP-OES analysis in 1-pentanol solution (50 mg/mL, with respect to the crude product) and in the solid crude product.

In the hardening (full hydrogenation) of vegetable oils and fats, in general, low reaction temperature, high turnover numbers, and good chemoselectivity are the driving economic and technology factors. Fatty oils, indeed, are complex mixtures of triglycerides which contain a broad spectrum of fatty acids, including saturated, monoenoic, and polyenoic FA. During hydrogenation, the composition becomes even more complex, as different double bonds show different reactivities. Furthermore, double bonds can shift along the carbon chain and also isomerize from *cis* to *trans* configuration, a serious healthy issue that has been addressed only most recently with the development of a shape selective solid Pt-based catalyst.[19]

Beyond their well-known action in cardiovascular diseases, *trans* fatty acids in the diet also have a detrimental effect on the brain and nervous system as they get incorporated into brain cell membranes, where these synthetic fats replace the natural DHA in the membrane, affecting the electrical activity of the neuron and its ability to communicate.[20] Replacement of Ni-based hydrogenation methods is thus of the uttermost urgency.

This and all the above requirements are met by the employment of Silia*Cat* Pd(0) in an ultrasmall amount under

Table 4. Full Hydrogenation of Vegetable Oils with Silia*Cat* Pd(0) under Mild Conditions[a]

entry	substrate	catalyst (mol %)	solvent (M)	time (h)	conv[b] (%)	leaching[c] (ppm)	
						Pd	Si
1	sunflower oil[7] (linoleic acid 64.5%, oleic acid 25.5%, and other 10%)	0.1	THF/MeOH (0.5 M)	3	99	0.3 (8.96)	0.19 (5.74)
2	sunflower oil (linoleic acid 64.5%, oleic acid 25.5%, and other 10%)	0.1	THF/MeOH (0.5 M)	2	99[d]	0.08 (1.68)	0.19 (3.80)
3	corn oil (linoleic acid 54%, oleic acid 27%, and other 19%)	0.1	THF/MeOH (0.5 M)	3	98	0.17 (3.31)	0.19 (3.82)
4	soybean oil (linoleic acid 50%, oleic acid 27%, linolenic acid 9%, and other 14%)	0.1	THF/MeOH (0.5 M)	3	99	0.52 (10.4)	0.42 (8.40)
5	canola oil (linoleic acid 22%, oleic acid 58%, linolenic acid 9%, and other 11%)	0.1	THF/MeOH (0.5 M)	3	99	0.36 (7.09)	0.165 (3.26)
6	olive oil (linoleic acid 8%, oleic acid 72%, and other 20%)	0.1	THF/MeOH (0.5 M)	2	99	0.32 (6.29)	0.19 (3.71)

[a]*Experimental conditions*: 14.5 mmol substrate in 30 mL of HPLC grade THF/MeOH 0.5 M with respect to the substrate (5:1 by volume ratio) over 0.1 mol % Silia*Cat* Pd(0) catalyst under hydrogen balloon room temperature conditions. [b]Conversion evaluated by TLC analysis (hexane/ethyl acetate = 5:1) using potassium permanganate stain and by ^{1}H RMN spectra in isolated crude product. [c]Leaching in Pd and Si determined by ICP-OES analysis in tetrachloroethane solution (50 mg/mL) and in solid crude product. [d]Reaction temperature 40 °C.

mild conditions while the catalyst, being a sol−gel doped silicate, can be easily scaled up.[21] A partner is sought in the oleochemical industry to carry out in co-operation a thorough economic and technical analysis on the use of Silia*Cat* Pd(0) under the mild conditions reported herein in place of state of the art Ni-based heterogeneous catalysis.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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