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Short Communication

# Platinum/3,3<sup>-</sup>-thiodipropionic acid nanoparticles as recyclable catalysts for the selective hydrogenation of *trans*-cinnamaldehyde



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# 1. Introduction

Catalysis by metal nanoparticles (NPs) has received a remarkable research effort as it stands at the frontier between homogeneous and heterogeneous catalysis, and attention has been focused on the recovery and reuse of these nanocatalysts. [1,2]. NPs have a large surface area-to-volume ratio compared to bulk materials, making them highly attractive for catalysis. For the preparation of stable metal NPs, various stabilizers have been used such as polymers, dendrimers, ligands, and surfactants.

Hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes such as cinnamaldehyde (CALD), is a challenge of high importance as hydrogenation of the C C bond leads to hydrocinnamaldehyde (HCALD) used in the flavouring industry [3] and in the synthesis of pharmaceuticals [4], while hydrogenation of the C O bond produces cinnamyl alcohol (CALH) used in the manufacture of perfumes [5]. A considerable attention has been focused on heterogeneous hydrogenation by metal NPs with the aim to remain both activity and selectivity [6–8]. The hydrogenation of the C O bond, and thus the reaction leads mainly to HCALD, but however, several noble metal NPs have been developed for the hydrogenation

#### ABSTRACT

Platinum nanoparticles as spherical aggregates were prepared by the reduction of a Pt(II) salt with hydrazine using 3,3'-thiodipropionic acid as a protective agent, and characterized by IR, XRF, XRD, and SEM where agglomerates have been visualized. The average crystallite size was 6 nm. For the first time such nanoparticles were evaluated as catalysts in the hydrogenation of unsaturated aldehydes. Hydrogenation of *trans*-cinnamaldehyde yielded cinnamyl alcohol with a selectivity of up to 83% at complete substrate conversion. At 30 °C, the catalyst could be recycled and reused for three runs with only slight losses in activity and selectivity.

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of the CO bond, and it is affected by several factors including the size of the NPs as the selectivity for CALH formation is increased by increasing their size [6–8]. Since the selectivity can be strongly dependent on the substrate conversion, high selectivity to CALH at high conversion level is a very important issue from a synthetic point of view. Amongst a large number of metal NPs for the hydrogenation of CALD, high selectivity towards CALH (>80%) at a high substrate conversion (>80%) has been reported by monometallic NPs such as Pt/PVP/FeCl<sub>3</sub> (conversion 84%: selectivity 99%) [9.10]. Pt/CTA/montmorillonite (89%: 80%) [11]. Pt/Na-Y (100%; 92%) [12], Pt/K-10 (96%; 96%) [13], Pt/SBA-15 (95%; 80%) [14], bimetallic NPs such as Pt-Fe/C (99%; 85%) [15], Co doped Pt nanocrystals (80%, >99%) [16], and also by bimetallic NPs on carbon nanotubes such as Pt-Co/CNTs (86%; 93%) [17] and Pt-Ru/CNTs (80%; 93-95%) [18-20]. These catalysts should be considered as the best metal NPs for the hydrogenation of CALD with respect to both high activity and selectivity towards CALH, but however, catalyst recycling and reusability were not investigated.

Herein, we report the preparation of platinum NPs by reduction of Pt(II) with hydrazine, using 3,3'-thiodipropionic acid (TDPC) as a protective agent (TDPC/Pt molar ratio = 0.1), and some preliminary results on the hydrogenation of CALD. TDPC has a strong affinity to the surfaces of metal NPs due to sulfur atoms, and gold, platinum and palladium small sized (<3.2 nm) as well as larger sized (37.2 nm) silver NPs with a very good stability for more than a half year, using TDPC as a protective agent, have previously been prepared by another process; Pt NPs for instance, were prepared by reduction of Pt(IV) with potassium



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Scheme 1. Preparation of Pt nanoparticles.

bitartrate, and the ratio of TDPC/Pt was 0.5–4.0 [21]. However, metal/ TDPC NPs as catalysts for the hydrogenation of unsaturated aldehydes have not been reported up to date.

# 2. Results and discussion

#### 2.1. Synthesis and characterization of platinum nanoparticles

The platinum NPs were prepared from sodium tetrachloroplatinate using tetraethylammonium chloride to extract  $PtCl_4^2$  into the organic phase (Scheme 1). Reduction of Pt(II) was achieved with aqueous hydrazine in the presence of TDPC, using a molar ratio TDPC/ Pt = 0.1. On addition of the reducing agent, the organic phase changed colour from yellow-orange to black-brown, indicating reduction of the platinum(II) ions. XRF analysis indicated 78% of Pt. In the IR spectrum of TDPC, the broad strong band at 2950 cm<sup>-1</sup> is assigned to the  $\nu(OH^{...}H)$  modes due to intermolecular H-bonding [22,23], and the strong band at 1695  $\text{cm}^{-1}$  corresponding to the vibration frequency v(CO) supports the intermolecular hydrogen bonds of the type CO<sup>...</sup>H-O in the uncoordinated TDPC. These bands are replaced by strong bands at 1626 and 1398  $cm^{-1}$  for the  $v_{asym}(COO)$  and  $v_{sym}(COO)$ , respectively, in the Pt NPs after deprotonation. The difference  $\Delta[\nu_{asym}(COO) - \nu_{sym}(COO)] = 228 \text{ cm}^{-1}$ is close to that found for the monodentate carboxylato group  $(230-240 \text{ cm}^{-1})$ . The  $\nu(CS)$  bands at 661 and 642 cm<sup>-1</sup> in the free TDPC are replaced by bands with a lower intensity in the Pt NPs, which are shifted to a lower frequency at 521 and 478  $\text{cm}^{-1}$ , respectively, suggesting interaction of platinum through sulfur [23,24].

The X-ray powder diffraction pattern of the Pt NPs is shown in Fig. 1. The three Bragg peaks are assigned to the Pt face-centered cubic (Fm-3m) phase. Crystallite size evaluation was carried out using the Scherrer equation where the mean nanocrystal size is derived from the peak width at half-maximum (FWHM). Line profile analysis was performed using the pseudo-Voigt fitting approximation. Crystallite sizes according to the measured FWHM values of each peak (111), (200), (220), were found 6.3, 5.9, and 5.8 nm,

respectively. The average crystallite size was therefore 6.0 nm. The similar values found across all Bragg angles indicate minimal strain broadening effects. It has previously been reported that the diameter of Pt NPs stabilized with TDPC is decreased by increasing the TDPC/Pt molar ratio with the largest size being 2.7 nm at TDPC/Pt molar ratio of 0.5 [21]. The NPs formed by a TDPC/Pt molar ratio of 0.1 as presented in this communication, have 6.0 nm crystallite size, which is in agreement with the above-mentioned observation, where it has been also suggested that the stabilizer inhibits the growth of NPs producing uniform particle size patterns [21].

Scanning electron microscopy (SEM) images of the Pt NPs (Fig. 2) reveal that they form spherical aggregates, which are approximately of uniform size. Minimum sizes resolved were in the range of 20–45 nm. The values obtained by powder diffraction patterns were smaller than the diameters observed in the SEM images where agglomerates have been visualized.

#### 2.2. Hydrogenation of trans-cinnamaldehyde

Preliminary results on the evaluation of Pt/TDPC NPs as catalysts in the hydrogenation of CALD are given below (Scheme 2, Table 1). Hydrogenations were carried out in ethanol with 1.9% NPs/CALD per weight (Pt/CALD molar ratio = 1:100) at 30 or 60 °C under 30 bar of hydrogen. In all experiments at a high or quantitative substrate conversion, the hydrogenation was highly selective towards the C O bond and the formation of CALH as the major product; HCALD (in some experiments) and HCALH were also formed. The formation of acetals, ethers or other side products was less than 1% or nonexistence as detected by <sup>1</sup>H NMR and GC–MS. As the temperature is increased from 30 to 60 °C, the conversion of CALD is increased at a reaction time of 6 h, while the selectivity for CALH is slightly decreased as part of CALH is further hydrogenated to HCALH (entries 3, 2). After 12 h at 30 °C, the conversion was quantitative with 83% selectivity for CALH (entry 4).

The feasibility of recycling the catalyst at 30 °C was also examined for three cycles (Fig. 3). After each cycle, the autoclave including the reaction mixture was cooled with an ice-water cooling bath, the supernatant solution was decanted and analyzed by GC, GC–MS and <sup>1</sup>H NMR, and the remaining nanocatalyst was dried under vacuum and used for the next cycle with only slight losses in activity and selectivity (entry 4).



Fig. 1. X-ray diffraction patterns of Pt(0) nanoparticles.



Fig. 2. SEM images of the of the Pt(0) nanoparticles at (a) low and (b) high magnification.



Scheme 2. Hydrogenation of trans-cinnamaldehyde and some characteristic <sup>1</sup>H NMR chemical shifts.

Since catalysis was performed by a Pt/CALD ratio of 1:100 under 30 bar of hydrogen affording TOFs of up to 16 h<sup>-1</sup>, the activity should not be considered as high as some other highly active Pt NPs for the hydrogenation of  $\alpha$ - and  $\beta$ -unsaturated aldehydes [6–8]. For instance, unsupported Pt/PVP/FeCl<sub>3</sub> NPs afforded TOF of 188 h<sup>-1</sup> for CALD hydrogenation under 40 bar of hydrogen; however, both the activity and the selectivity for CALH dramatically drop down without the metal cation as a promoter [9,10]. A higher activity compared to our catalyst is also achieved by several supported NPs, such as Pt/CTA/ montmorillonite with TOF of 130  $h^{-1}$  under 5 bar of hydrogen [11], and Pt-Ru bimetallic NPs on carbon nanotubes with TOFs of up to  $356 h^{-1}$  under 20 bar of hydrogen [20]. However, it is noteworthy to mention that although the majority of unsupported monometallic NPs without any promoter exhibit higher selectivity on CC hydrogenation providing the saturated aldehyde, at a complete substrate conversion the presented Pt/TDPC NPs display comparable or somewhat lower selectivity for the formation of the unsaturated alcohol as other highly selective systems [9–20]. The good stability of the Pt/TDPC NPs as uniform sized spherical aggregates with a relatively large size could lead to steric

Table 1	
Hydrogenation of <i>trans</i> -cinnamaldehyde catalyzed by Pt/TDPC nanoparticles. <sup>a</sup>	

Entry	T (°C)	Time (h)	Conversion (%) <sup>b</sup>	TON/ TOF(h <sup>-1</sup> ) <sup>c</sup>	Selectivity (%) <sup>b</sup> CALH/HCALD/HCALH
1	60	12	>99	99/8.3	77:-:23
2	60	6	96	96/16.0	79:6:15
3	30	6	87	87/14.5	82:7:11
4	30	12	>99 (cycle 1)	99/8.3	83:-:17 (cycle 1)
			98 (cycle 2)	98/8.2	83:4:13 (cycle 2)
			95 (cycle 3)	95/7.9	78:7:15 (cycle 3)

<sup>a</sup> Reaction conditions: Pt/CALD molar ratio = 1:100; EtOH;  $P(H_2) = 30$  bar.

<sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy.

<sup>c</sup> TOF = Moles of CALD transformed per mole of Pt per hour.

constraints for C C bond approach to the surface in contrast to C O bond, and thus could contribute to the selective C O hydrogenation.

#### 3. Conclusions

In conclusion, platinum nanoparticles as approximately uniform sized spherical aggregates have been prepared using 3,3'-thiodipropionic acid (TDPC) as a protective agent. The process displays differences from the previously reported method for the synthesis of Pt/TDPC nanoparticles, concerning the starting platinum salt (Pt(II) instead of Pt(IV)), the reductant (hydrazine instead of potassium bitartrate), and the TDPC/Pt molar ratio (0.1 instead of 4.0–0.5) offering the possibility of increasing their crystallite size to 6 nm instead of 1.0–2.7 nm in the previous report. For the first time such nanoparticles were used



Fig. 3. Conversion of CALD and selectivity for CALH by the catalyst recycling.

as catalysts in the hydrogenation of *trans*-cinnamaldehyde, an important reaction of academic and industrial interest, and provided promising preliminary results. Although the activity is not as high as several other very reactive catalytic systems for this reaction, the selectivity towards cinnamyl alcohol was found to be of up to 83% at complete substrate conversion, comparable or somewhat lower with the most selective platinum catalysts described in the literature. The sedimentation of these nanoparticles opened a route to easy recycling, and thus, at 30 °C the nanocatalyst could be recycled and reused for three runs with only slight losses in activity and selectivity as an important additional benefit. This first study concerning the use of monometallic Pt/TDPC nanoparticles on the hydrogenation of cinnamaldehyde provides important information on the catalytic activity of these systems.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2013.09.008.

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