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Platinum supported on TiO$_2$ as a new selective catalyst on heterogeneous hydrogenation of α,β-unsaturated oxosteroids

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ABSTRACT

This paper describes the photochemical deposition of platinum onto TiO$_2$ surface and the full characterization of the catalysts using BET, XPS and TEM techniques. The 1 and 3 wt. % Pt/TiO$_2$ catalysts reveal high activity with 70% and 96% of α-diastereoselectivity in the hydrogenation of the carbon–carbon double bond of the α,β-unsaturated oxosteroids 4-androstene-3,17-dione, and 3β-acetoxypregna-5,16-dien-20-one, respectively. Using higher temperature and pressure, the catalysts promote the further reduction of C-3 carbonyl group. Catalyst recovering and recycling is easily achieved with no appreciable lost of catalytic activity after five subsequent runs.

1. Introduction

Chemo-selective hydrogenation of multi-unsaturated molecules over heterogeneous catalysts is a demanding task [1–4]. The polyfunctionalization of the steroidal framework, for example, is a stimulating stereochemical exercise in synthetic chemistry. The complexity and diversity of functional groups endow these molecules with their diverse biological properties, namely as hormones and vitamins [5]. The characterization of the receptors and enzymes involved in the biosynthesis and metabolism of these compounds engaged the synthetic chemist on the optimization and development of stereoselective processes. Therefore, the chemo and diastereoselective hydrogenation of unsaturated steroids remains an important field due to the potentiality of this process to synthesize steroidal bioactive molecules and metabolites.

In the literature, several approaches are reported to perform the selective reduction of steroidal conjugated enones and dienones by using metal–ammonia solutions [6,7] and catalytic processes, either homogeneous [8,9], heterogeneous [10–14] or by linking homogeneous catalysts onto solid supports [15]. Due to easily catalyst recovery, heterogeneous catalysts have been extensively employed in steroid hydrogenation, namely palladium supported on carbon [16]. Also, heterogeneous catalysts serve the purpose of diastereo- [17,18] and enantioselective [19] reduction of carbonyl groups in the steroidal framework.

The diastereoselectivity of these hydrogenation reactions depends on the mode of substrate adsorption 1,2 *versus* 1,4 to the catalytic active site, which can be modulated by metal, support, solvent polarity and pH [16,20–24]. In general, heterogeneous reduction of Δ^4-3-ketosteroids produces mainly the 5β-isomer [25–27], while the homogeneous or supported homogeneous catalytic processes allow the opposite α-selectivity [5,8,28].

Titanium dioxide can be used as a catalyst itself, photocatalyst under UV light in the degradation of organic pollutants [29–33], or as a support for heterogeneous catalyst preparation. In this field, noble metals, especially platinum, have been used to some extent. The possibility of taking advantage of the strong metal support interaction (SMSI) effect, after high temperature reduction, certainly makes TiO$_2$ a very interesting support for hydrogenation reactions [34].

The photochemical deposition is an efficient method for metal deposition over semiconductor materials [35,36], which was successfully applied in the recovery of noble metals from wastewaters under UV light [30,32], and can be used as an alternative tech-

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nique to the preparation of noble metal supported catalysts. Its main advantage resides on the ability of spreading very effectively the metal throughout the support, thus normally leading to high dispersions. Additionally, when a semiconductor, like TiO_2, is used as support the photodeposition process also results in simultaneous reduction of the metal ions by conduction band electrons. The latter can be further enhanced by addition of certain substances said sacrificial electron donors that can supply an almost unlimited amount of electrons and, thus, improve the rate of photodeposition. Among the most commonly used are formaldehyde, methanol and 2-propanol [37].

In the present study we report the photochemical deposition of platinum into TiO_2 and the full characterization of the catalyst. These heterogeneous catalyst presented high activity and selectivity for the carbon–carbon double bond hydrogenation of the α,β-unsaturated oxosteroids 4-androstene-3,17-dione, **1**, and 3β-acetoxypregna-5,16-dien-20-one, **2**.

2. Experimental

2.1. Equipments and reagents

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on Bruker Avance 300 operating at 300.13 for ^{1}H and 75.47 MHz for ^{13}C. TMS was used as internal reference. GC and GC–MS experiments were carried out on Agilent 6890 series equipped with capillary Agilent HP5 columns with 30 m and 0.5 m respectively, and identification of products was carried out against standards [15,28].

Solvents were obtained from commercial sources (Aldrich) distilled and dried before use, according to standard procedures [38].

Specific BET surface areas (S_{BET}) were calculated based on the nitrogen adsorption–desorption isotherms determined at $-196\,°C$ with a Coulter Omnisorp 100CX apparatus. The samples were outgassed for at least 4 h at 150 °C, before allowing them to cool down in vacuum to ambient temperature.

The metal dispersion was determined by H_2 chemisorption at room temperature in an U-shaped tubular quartz reactor after a thermal treatment to remove contaminant species from the catalyst surface. Pulses of H_2 were injected through a calibrated loop into the sample at regular time intervals until the area of the peaks became constant. The amounts of H_2 chemisorbed were calculated from the areas of the resultant H_2 peaks. The H_2 was monitored with a SPECTRAMASS Dataquad quadrupole mass spectrometer.

Transmission electron microscopy (TEM) observations were made with a LEO 906 E from LEICA (120 kV voltage). The samples were dispersed in ethanol and collected on a copper carbon-coated TEM grid.

Surface analysis for topographical and analytical characterization was carried out by scanning electron microscopy (SEM) with a JEOL JSM-6301F (15 keV) electron microscope equipped with an OXFORD INCA ENERGY 350 energy dispersive X-ray spectroscopy (EDS) system. The sample powders were mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes, secondary and back-scattered electrons.

X-ray photoelectron spectroscopy (XPS) was used to determine the surface atomic composition of platinum supported catalysts in a VG Scientific ESCALAB 200A spectrometer using a non-monochromatized AlKα radiation (1486.6 eV). The sample powders were mounted directly on a double-sided adhesive tape. The pressure in the analysis chamber was inferior to 10^{-8} mbar during data collection. Binding energy (BE) spectra were recorded in the regions of O_{1s}, Ti_{2p}, and Pt_{4f}. The spectra thus obtained were analyzed by XPSpeak 4.1 software by deconvoluting the peaks with mixed Lorentzian–Gaussain functions after a Shirley background subtraction.

2.2. Catalyst synthesis

Titania supported platinum catalysts with different metal loadings, 1 and 3 wt. % (1Pt/TiO_2 and 3Pt/TiO_2, respectively), were prepared by the photochemical deposition method. The aqueous solutions containing the desired amounts of methanol (Riedel-de Haën, 99.8), dihydrogen hexachloroplatinate (IV) (Alfa Aesar, 99.9%) and titanium dioxide (P-25, Evonik previously Degussa) were sonicated for 30 min to prevent particle agglomeration. The suspensions were then irradiated by a low-pressure mercury lamp with an emission line at 253.7 nm (ca. 3 W of radiant flux) for 4 h. The catalysts were then recovered by filtration and dried in oven at 90 °C for 2 days [35]. A 500 °C thermal treatment was applied to the catalysts, consisting of calcination under nitrogen (N_2, 4 h, 100 mL min^{-1}), reduction with hydrogen (H_2, 2 h, 20 mL min^{-1}) and finally flushing again with N_2 for 30 min in order to remove physisorbed hydrogen, and stored in a desiccator until further use. The platinum loaded to the support was controlled indirectly by monitoring the 261 nm band of the rinsing water using an UV–vis spectrometer (Jasco V560).

A 10 wt. % Pd/C commercial (10Pd/C, extent of labeling: 10 wt. % loading in a dry basis, matrix activated carbon, wet support, Degussa type E101 NE/W, Sigma–Aldrich 330108) was used as benchmark catalyst for the reduction of 4-androstene-3,17-dione.

2.3. Hydrogenation procedure

The substrate (0.07 mmol) and the catalyst were introduced in the autoclave. The system was sealed and then purged with three H_2/vacuum cycles, after which toluene (10 mL) was introduced through an inlet cannula. The reaction mixture was heated to the required temperature and then the system was filled with desired H_2 pressure. After reaching the desired temperature and pressure, stirring was initiated. The conversions and selectivity were determined by gas chromatography.

2.3.1. Reduction of 4-androstene-3,17-dione and 3β-acetoxy-pregna-5,16-diene-20-one

4-Androstene-3,17-dione (**1**) and 3β-acetoxy-pregna-5,16-diene-20-one (**2**) were submitted to heterogeneous catalytic hydrogenation according to the general procedure described above. When the catalytic reaction was stopped, the reactor was cooled and depressurized. Evaporation of toluene afforded a crude that was submitted to silica gel preparative column chromatography using CH_2Cl_2:AcOEt (9:1) as eluent.

5α-H-androstan-3,17-dione **1.1** and 3β-acetoxy-17α-H-pregn-5-ene **2.1** were isolated and characterized. Data is in good agreement with the previously reported one [15,28].

2.4. Catalyst recycling

After each run, the reactor was opened to air. Catalyst recovery was performed by filtration of the solid from the reaction mixture. Then, the catalyst was reintroduced in the reactor and purged. A fresh substrate solution, in toluene, was introduced *via* an inlet cannula. The catalytic reaction conditions described above were used to perform the subsequent catalytic cycles.

3. Results and discussion

3.1. Catalyst characterization

P-25 titanium dioxide from Evonik was used throughout this study and consists of an anatase/rutile (A/R) crystalline ratio of

Table 1
Specific BET surface area (S_{BET}), platinum particle size (d_{Pt}), load (y_{Pt}) and amount of reduced platinum ($Pt^{(0)}$) for TiO_2 supported catalysts.

Catalyst	S_{BET} ($\pm 5\,m^2\,g^{-1}$)	d_{Pt}[a] ($\pm 0.2\,nm$)	d_{Pt}[b] ($\pm 5\,nm$)	y_{Pt} ($\pm 0.05\,wt.\%$)	$Pt^{(0)}$ ($\pm 3\%$)
TiO_2	32.3	–	–	–	–
$1Pt/TiO_2$	32.9	4.0	30	1.03	66
$3Pt/TiO_2$	34.8	5.4	73	3.02	91

[a] Determined by TEM analysis.
[b] determined by H_2 chemisorption.

80/20, surface area of $32\,m^2\,g^{-1}$ and particle size ca. 22 nm. Due to the production mechanism of this material TiO_2 is essentially non-porous with all the observed surface area due to adsorption on the external surface. A certain load of Pt (1–3 wt. %) was deposited on the surface by the photochemical method. Table 1 summarizes catalyst specific BET surface areas, platinum particle size (according to TEM analysis and hydrogen chemisorption), load (EDS semi-quantitative analysis) and oxidation state (XPS analysis). For each sample analyzed a minimum of 3 reproducible measurements was considered.

Textural analysis of platinum catalysts did not reveal any significant changes to the specific BET surface area, as the values are very similar to that of the naked TiO_2 support.

The Pt load agrees with the targeted amounts and in spite of EDS being a surface technique, since the support is non-porous, the determination offers a good representation of the real load. In addition, UV–vis analysis of the aqueous solution used in deposition, confirmed that the full amount of metal was deposited.

The particle size determined by H_2 chemisorption measurements (Table 1) is considerably larger than that determined by TEM analysis. These differences can be explained considering the existence of a strong metal support interaction (SMSI) effect [34], where the surface becomes decorated with sub-stoichiometric TiO_x moieties hindering H_2 chemisorption to the noble metal. Hence, the difference in particle size is attributed to a H_2 chemisorption blockage instead of a sintering effect by the metallic phase (Fig. 1).

According to XPS data no noticeable differences were observed in the Ti 2p and O 1s characteristic regions between the naked and Pt containing samples. The Ti 2p region was composed by the $2p_{3/2}$ and $2p_{1/2}$ doublet. The binding energy of Ti $2p_{3/2}$ peak was centered at 459.5, which can be assigned to Ti(IV), indicating that the Ti exists in the form of TiO_2. The peak centered at 530.4 eV was in good agreement with O 1s electron binding energy for oxygen bound to tetravalent Ti ions. For Pt, the XPS Pt 4f region can be resolved into two pairs of doublets (Pt $4f_{7/2}$ at lower and Pt $4f_{5/2}$ at higher binding energies). The XPS Pt $4f_{7/2}$ region shows a band that can be deconvoluted into a peak centered at 71.3 eV assigned to Pt(0) (66% for $1Pt/TiO_2$ and 91% for $3Pt/TiO_2$), and other peak centered at 74.3 eV assigned to Pt(II), most likely in the form of PtO. All platinum peaks were resolved according to the constraint that the Pt $4f_{5/2}$ and Pt $4f_{7/2}$ ratio was 6.81/8.65 [39].
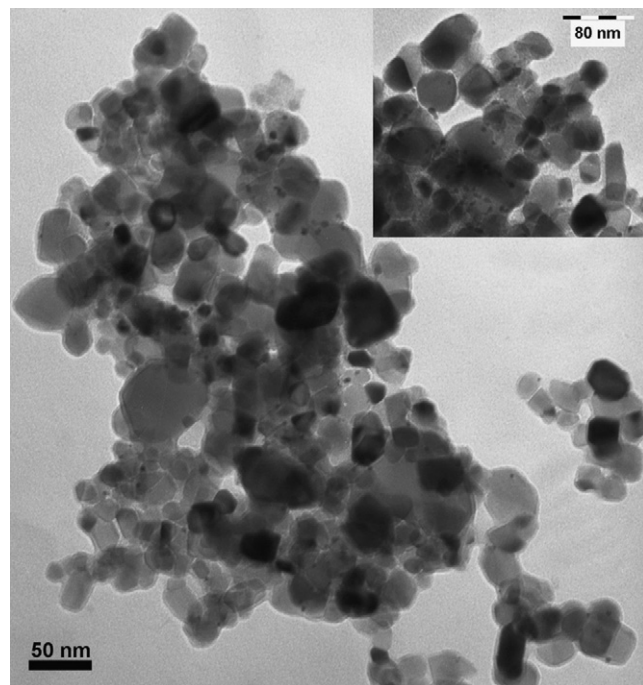
Fig. 1. TEM micrograph of $1Pt/TiO_2$ catalyst. Inset: alternative view of the same material at different magnification.

### 3.2. Catalytic hydrogenation of α,β-unsaturated oxosteroids

In order to evaluate the activity and selectivity of the Pt/TiO_2 catalysts, the hydrogenation of steroid **1** was performed with the widely used and commercially available 10Pd/C catalyst (entry 6, Table 2) and with the two different Pt/TiO_2 catalysts, at different values of temperature and pressure (Scheme 1a). The results are collected in Table 2.

To perform the catalytic reaction, the suitable amount of $3Pt/TiO_2$ catalyst and substrate **1**, dissolved in toluene, were introduced in the autoclave, at 100 °C and 20 bar H_2. Gas chromatography analysis of aliquots, from the reaction mixture, showed 97% conversion with 95% of chemoselectivity for carbon–carbon

Table 2
Conversion and selectivity of the hydrogenation reactions [Pt] = 3.0×10^{-3} mmol; solvent: toluene (2 mL); substrate/M = 35 under several conditions of steroids **1** and **2**.

Entry	Steroid	Catalyst	$P\,H_2$ (bar)	T (°C)	Time (h)	Conversion (%)	Chemo selectivity (%)	Diastereo selectivity (%)
1	**1**	$3Pt/TiO_2$	20	100	1/12	97	95 (**1.1 + 1.2**)	71 (**1.1**)
2	**1**	$3Pt/TiO_2$	20	30	1/2	94	95 (**1.1 + 1.2**)	70 (**1.1**)
3	**1**	$3Pt/TiO_2$	5	30	1/2	96	97 (**1.1 + 1.2**)	70 (**1.1**)
4	**1**	$1Pt/TiO_2$	5	30	1/2	45	97 (**1.1 + 1.2**)	73 (**1.1**)
					2	98	96 (**1.1 + 1.2**)	75 (**1.1**)
5	**1**	$1Pt/TiO_2$	20	100	8		85 (**1.3**)	
6	**1**	10Pd/C	5	30	1/2	80	97 (**1.1 + 1.2**)	54 (**1.1**)
7	**2**	$1Pt/TiO_2$	5	30	1	99	96 (**2.1**)	
8	**2**	$1Pt/TiO_2$	20	100	17		79 (**2.2**)	
9	**2**	TiO_2	5	30	2	0	– (**2.2**)	

Key for number designation in Scheme 1.
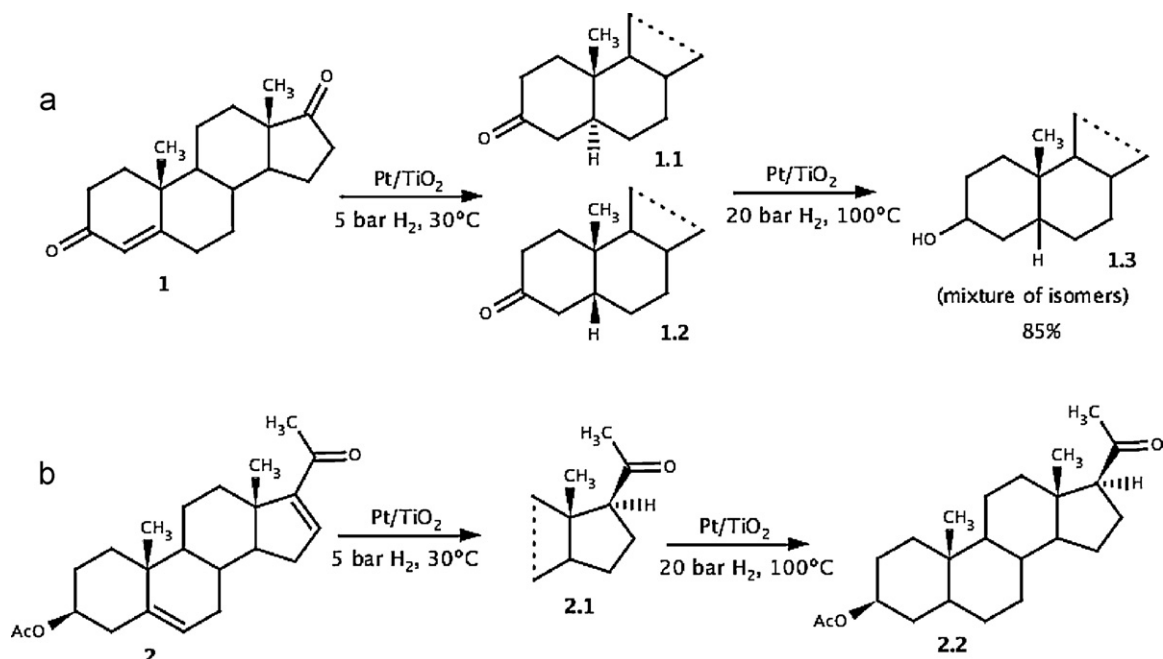
Scheme 1.

double bond reduction and 71% of α-diastereoselectivity, after 5 min (entry 1, Table 2). To investigate the effect of temperature on the selectivity of the catalytic system the temperature was decreased to 30 °C keeping the same pressure (entry 2, Table 2). Even at this low temperature 3Pt/TiO$_2$ showed high activity, 94% after 30 min, but selectivity remained unchanged. The effect of pressure on the activity and selectivity is negligible, as seen by decreasing the hydrogen pressure from 20 bar (entry 2, Table 2) to 5 bar (entry 3, Table 2) while the activity and selectivity are unchanged.

The effect of the amount of platinum adsorbed to TiO$_2$ was also studied. The hydrogenation of steroid **1**, with 1Pt/TiO$_2$, applying the milder reaction conditions (30 °C and 5 bar), produced an almost complete conversion, after 2 h, with the same selectivity as 3Pt/TiO$_2$ (entries 4 and 3, Table 2, respectively).

It is also relevant to notice that when the hydrogenation of steroid **1** is performed with substrate:catalyst = 300 (1Pt/TiO$_2$; 30 °C and 5 bar) an almost complete conversion was obtained with the same selectivity, after 26 h.

When the α,β-unsaturated oxosteroid **1** was submitted to more drastic reaction conditions (100 °C, 20 bar H$_2$) in the presence of 1Pt/TiO$_2$, the carbonyl group at C-3 of the steroid ring was reduced to the corresponding alcohols (85%), after 8 h (entry 5, Table 2). Product characterization by ^{1}H NMR, put in evidence that equatorial alcohols are predominantly formed (70%). Such outcome shows that this heterogeneous catalytic system allows a similar selectivity to the homogeneous rhodium-diphosphite catalyst but is significantly more active [28].

In order to compare the activity and selectivity of the new catalyst (3Pt/TiO$_2$ entry 3, Table 2) with the commercial 10Pd/C (entry 6, Table 2), steroid **1** was submitted to the same hydrogenation conditions (5 bar; 30 °C). The activity of both catalysts is similar but the α-diastereoselectivity with 3Pt/TiO$_2$ is significantly higher.

To estimate the activation energy, the reaction was carried out at different temperatures (from 30 to 50 °C), at a constant pressure of 5 bar H$_2$ and five or more aliquots were taken until complete conversion was reached. From an Arrhenius plot of $\ln(k)$ as function of $1/T$, the value of 78.4 kJ mol^{-1} was obtained for the apparent activation energy. This rather high value strongly supports the involvement

of a chemical adsorption step in the mechanism. Thus, the somewhat unexpected high diastereoselectivity registered can result of a differentiated adsorption of the conjugated functional groups in the catalytic centre and its vicinity. In the case of the Pt catalyst due to the SMSI effect (by which partial coverage of the metal centre takes place), the alkene function is adsorbed in such a preferential geometry that leads to the formation of the less hindered diastereoisomer.

The 1Pt/TiO$_2$ catalyst was also used in the heterogeneous catalytic hydrogenation of $\Delta^{5,16}$-oxosteroid **2**, at hydrogen pressure of 5 bar and temperature of 30 °C (Scheme 1b). After 1 h, 99% conversion was achieved, with 100% regioselectivity for the Δ^{16} double bond reduction and 97% of α-diastereoselectivity (entry 7, Table 2). When the same substrate **2** was submitted to stronger hydrogenation conditions (20 bar and 100 °C) and longer reaction time (17 h), both Δ^{16} and the very hindered Δ^5 double bonds were reduced, as confirmed by ^{1}H and ^{13}C NMR (entry 8, Table 2). Even at this more drastic reaction conditions, the 20 –CO group remains unchanged.

To evaluate the catalytic activity of the support TiO$_2$, a blank run was carried out (5 bar and 30 °C) using substrate **2**. No reduction of the less hindered Δ^{16} double bond was observed after 2 h, which puts in evidence that the refractory material TiO$_2$ does not present any catalytic effect (entry 9, Table 2).

3.3. Catalyst recycling

The recovery of the catalyst for reuse is of utmost environmental and economical relevance, especially in diastereoselective processes. In this context, using substrate **1**, as model, we have also assessed the effect of reusing the heterogeneous 3Pt/TiO$_2$ catalyst on the activity and selectivity of the hydrogenation reaction. Thus, after each catalytic run, the reactor was opened to the air. The catalyst was then filtered and reintroduced in the reactor, concomitantly with a new amount of substrate, keeping the aforementioned catalyst/substrate ratio. The catalyst performance remains unchanged after five subsequent runs (Fig. 2). It is noteworthy that in all the catalytic cycles the chemoselectivity and diastereoselectivity were not affected upon reutilization. Recycling
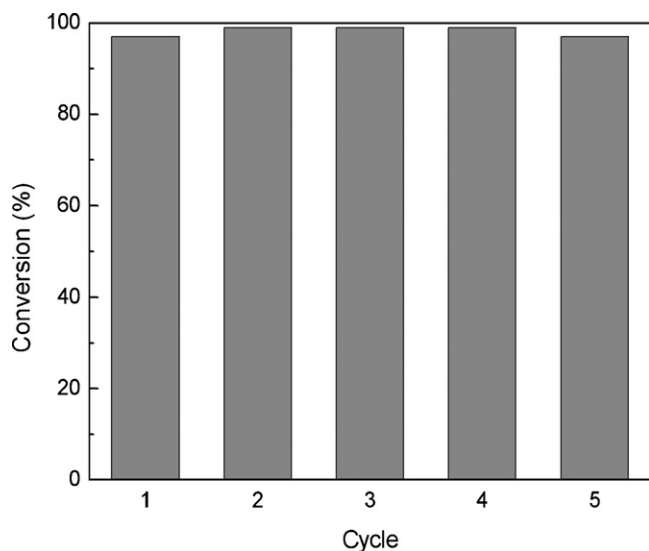
Fig. 2. Activity of the 3Pt/TiO$_2$ catalyst after 5 subsequent runs.

studies were also carried out in the catalytic hydrogenation of substrate **2** and similar results were obtained.

4. Conclusions

The photochemical deposition method proved to be quite simple and effective to produce TiO$_2$ supported Pt nanoparticles in the range of 4–5 nm, depending on the metal load present. The catalytic materials showed high activities and selectivities for the hydrogenation of α,β-unsaturated oxosteroids in extremely mild conditions (30 °C and 5 bar of hydrogen). The activity and selectivity of these catalysts are pressure independent, in the studied interval. However, the regioselectivity can be modulated by the temperature of the catalytic process, *i.e.* it was possible to selectively reduce the less hindered Δ^4 or Δ^{16} double bonds at almost room temperature (30 °C) but higher temperatures (100 °C) allowed the reduction of the more hindered Δ^5 double bond and/or the carbonyl group.

The α-diastereoselectivity was outstanding, being comparable to the homogeneous process. Such a result must be emphasized as, according to the literature, surface unmodified heterogeneous catalysts provide low diastereoselectivities, with broad predominance of the β-isomer.

This new TiO$_2$ supported platinum catalyst has a high potential for industrial application as it can be reused at least 5 cycles without loosing activity or selectivity.

Acknowledgments

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