Journal of Molecular Catalysis A: Chemical 333 (2010) 1–5

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Editor's choice paper

Platinum supported on TiO_2 as a new selective catalyst on heterogeneous hydrogenation of α,β-unsaturated oxosteroids

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ARTICLE INFO

Article history:
Received 2 June 2010
Received in revised form
25 September 2010
Accepted 28 September 2010
Available online 7 October 2010

Keywords:
Heterogeneous
Hydrogenation
Unsaturated oxosteroid
Platinum

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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doi:10.1016/j.molcata.2010.09.019

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

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on Bruker Avance 300 operating at 300.13 for ^1H 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