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Platinum nanoparticles supported on titania as an efficient hydrogen-transfer catalyst

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ABSTRACT

Platinum(0) nanoparticles supported on titania have been prepared by impregnation of a commercial TiO_2 support with an aqueous solution of H_2PtCl_6 and further reduction under flowing H_2 at 473 or 773 K. These materials, with a low platinum loading, have been found to effectively catalyze the reduction of acetophenone by hydrogen transfer, using isopropanol as the hydrogen donor, in the presence of potassium hydroxide at 349 K. To the best of our knowledge, this is the first time that a supported platinum catalyst has been successfully used in the transfer hydrogenation of carbonyl compounds with isopropanol. Both catalysts could be reused several times, with the one reduced at 773 K exhibiting better catalytic performance than that reduced at 473 K.

1. Introduction

Interest continues in the reduction of carbonyl compounds to the corresponding alcohols as a fundamental and common functional group transformation in synthetic organic chemistry. Among the different methodologies used to carry out this reaction, four important general procedures can be highlighted that involve the use of metal hydrides, dissolved metals, catalytic hydrogenation, and transfer hydrogenation [1,2]. Other methods, such as electrochemical or enzymatic methods, are of less practical application. Hydrogen transfer reactions [3–6] are advantageous with respect to other reduction methods because of several reasons: (a) the hydrogen donor is easy to handle (no gas containment or pressure vessels are necessary), cheap and environmentally friendly (e.g., isopropanol); (b) possible hazards are minimized; (c) the mild reaction conditions applied can afford enhanced selectivity; and (d) catalytic asymmetric transfer hydrogenation can be applied in the presence of chiral ligands [7,8].

The transfer hydrogenation of ketones has been mostly accomplished using isopropanol as a hydrogen donor under homogeneous conditions in the presence of noble metal complexes. The most efficient catalysts devised so far are based on second- or third-row transition metals in d^6 or d^8 electronic configuration, with Ru [9], Rh [10], and Ir [11] complexes apparently more active than comparable Pd, Pt, and Os derivatives. In fact, ruthenium complexes have been by far the most widely studied catalysts, especially for the asymmetric transfer hydrogenation of aromatic ketones [12–14] and from a mechanistic standpoint [15–17]. Less attention has been given to the hydrogen transfer reduction of carbonyl compounds under heterogeneous conditions, however.

The use of heterogeneous catalysts offers several advantages over the homogeneous systems, including easy recovery, easy recycling, and enhanced stability [18]. In this sense, we have recently reported the application of reusable nickel nanoparticles [19,20] to the hydrogen transfer reduction of carbonyl compounds [21,22] and to the hydrogen transfer reductive amination of aldehydes [23] with isopropanol.

On the other hand, Pt/TiO_2 catalysts have been extensively used in hydrogenation reactions involving carbonyl groups. Tauster et al. showed that when used as a support, TiO_2 can significantly modify the chemisorption behavior of noble metals after reduction at high temperature (773 K) [24,25]. Later, Vannice et al. [26] found that titania-supported catalysts were more active in CO hydrogenation after reduction at high temperature, and that the behavior was similar in other reactions in which a carbonyl group was hydrogenated. Recent works have reported the catalytic behavior of Pt/TiO_2 catalysts in the vapor-phase hydrogenation of α,β-unsaturated aldehydes, such as crotonaldehyde [27–31] and cinnamaldehyde [32], to obtain the corresponding unsaturated alcohols, as well as in the hydrogenation of other compounds, such

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as acetophenone [33] and benzaldehyde [34]. In all cases, the turnover frequencies for the hydrogenation of the carbonyl group after reduction at high temperature were much higher than those obtained after reduction at lower temperature (473, 523 K). This finding has been explained on the basis of the creation of new active sites at the interface between the metal particles and patches of partially reduced support.

It is noteworthy that platinum catalysts have been scarcely applied in hydrogen transfer reactions. For instance, the photocatalytic transfer hydrogenation of imines with isopropanol was achieved with suspended semiconductor particles loaded with platinum deposits [35]. But this transfer hydrogenation required both photoirradiation (>300 nm) and suspended semiconductor particles (CdS). Platinum supported on carbon exhibited low catalytic activity compared with other carbon-supported noble metal catalysts in the hydrogen transfer hydrodechlorination of 1,2,4-trichlorobenzene with isopropanol [36]. Platinum catalysts supported on γ-Al_2O_3 and on various zeolites were shown to be active in the transfer hydrogenation of propylene using butanes as the hydrogen source [37]. Aromatic nitro compounds were reduced to the corresponding anilines using 5% Pt/C with ammonium formate or formic acid as hydrogen donors [38]. To the best of our knowledge, however, an effective platinum-catalyzed hydrogen transfer reduction of carbonyl compounds with isopropanol as hydrogen source has not been reported to date. In this context, this paper reports the preparation and characterization of platinum nanoparticles supported on titania submitted to different reduction treatments, along with their catalytic behavior and reusability in the hydrogen transfer reduction of acetophenone.

2. Experimental

2.1. Catalyst preparation

A commercial TiO_2, Degussa P25, (60% anatase, 40% rutile), with a surface area of 50 $m^2\,g^{-1}$ (N_2, 77 K, BET method), previously calcined in air at 773 K for 5 h, was used as a support. The Pt/TiO_2 catalyst was prepared by an impregnation method with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (Johnson Matthey) of the appropriate concentration to achieve a Pt content of 1.5 wt%. The slurry (10 $ml\,g^{-1}$ of support) was stirred for 12 h, after which the excess solvent was removed by heating at 363 K under vacuum in a rotary evaporator. Finally, the catalyst was dried at 383 K for 24 h and calcined under a flow of synthetic air at 673 K for 4 h, at a heating rate of 5 $K\,min^{-1}$.

2.2. Catalyst characterization

TEM images were obtained with a JEOL JEM-2010 microscope using an acceleration voltage of 200 kV. The catalyst was previously reduced *ex situ* under hydrogen flow (50 $cm^3\,min^{-1}$) at 473 and 773 K for 1 h. After reduction, the catalyst was placed on a copper grid using suspensions in ethanol.

XPS spectra were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a MgK_α 300 W ($h\nu = 1253.6$ eV, 1 eV $= 1.6302 \times 10^{-19}$ J) 300 W X-ray source. The powder samples were pressed into small Inox cylinders and then mounted on a sample rod placed in a pretreatment chamber and reduced in H_2 for 1 h at 473 and 773 K before being transferred to the analysis chamber. Before the spectra were recorded, the sample was maintained in the analysis chamber until a residual pressure of 3.75×10^{-9} Torr was reached. The spectra were collected at a pass energy of 50 eV. The intensities were estimated by calculating the integral of each peak after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. Binding energies were referenced to the Ti $2p_{3/2}$ line in the TiO_2 at 458.5 eV, providing values with an accuracy of ±0.2 eV. The surface Pt/Ti ratios were estimated from the integrated intensities corrected for atomic sensitivity factors [39].

Microcalorimetric measurements of CO adsorption were performed at 298 K using a Setaram BT2.15D heat-flux calorimeter. The calorimeter was connected to a manometric system using a Baratron capacitance manometer for precision pressure measurement (±0.001 Torr). The maximum leak rate of the volumetric system (including the calorimetric cell) was 10^{-5} $Torr\,min^{-1}$ in a system volume of approximately 60 cm^3. The sample (between 0.25 and 0.6 g) was reduced *ex situ* in high-purity hydrogen (50 $cm^3\,min^{-1}$) at 473 or 773 K for 1 h. After reduction, the sample was outgassed at the reduction temperature for 15 min, then purged at the same temperature for 1 h in high purity helium to remove any adsorbed hydrogen. Then it was sealed in a Pyrex NMR tube and placed in a special calorimetric cell. When thermal equilibrium was reached, the capsule was broken, and small pulses of CO were introduced until the saturation was achieved. The resulting heat response for each pulse was recorded as a function of time and integrated to determine the energy released. The differential heat ($kJ\,mol^{-1}$) was defined as the negative of the enthalpy change of adsorption per mole of gas adsorbed.

2.3. Catalytic experiments

The catalyst (0.1 g) was reduced *ex situ* in high-purity hydrogen (50 $cm^3\,min^{-1}$) at 473 or 773 K for 1 h. After reduction, the sample was outgassed at the reduction temperature for 15 min, then purged at the same temperature for 1 h in high-purity helium to remove any adsorbed hydrogen. Then it was sealed in a Pyrex NMR tube. The capsule was broken in isopropanol to avoid air contamination. KOH (56 mg, 1 mmol, from Alfa Aesar) and acetophenone (117 µl, 1 mmol, from Acros) were added successively over the suspension of 1.5% Pt/TiO_2 (100 mg, 0.0077 mmol Pt, 0.8 mol% referred to acetophenone) in isopropanol (4 ml; from Acros) under argon. The reaction mixture was warmed up to 349 K and monitored by GLC and/or GC-MS until steady conversion of the starting material was achieved. The resulting suspension was filtered through a pad containing celite, the filtrate was dried over $MgSO_4$, and the solvent was evaporated at reduced pressure (15 Torr). The resulting residue was subjected to GLC analysis to determine the yield of the product 1-phenylethanol. Catalyst reuse was carried out by decantation, supernatant removal, three washes with isopropanol, and addition of more isopropanol, KOH, and acetophenone.

The chromatographic analyses (GLC) were determined with a Hewlett Packard HP-5890 instrument equipped with a flame ionization detector and a 30-m HP-1 capillary column (0.20 mm internal diameter, 0.2 µm film thickness), using nitrogen (2 $ml\,min^{-1}$) as the carrier gas, $T_{injector} = 548$ K, $T_{column} = 333$ K (3 min), and 333–548 K (15 $K\,min^{-1}$). Alternatively, the reaction course also was followed by GC-MS at 70 eV on Shimadzu QP-5000 and Agilent 5973 spectrometers, equipped with a 12-m HP-1 capillary column (0.2 mm internal diameter, 0.25 µm film thickness).

3. Results and discussion

3.1. Characterization of the Pt/TiO_2 catalysts

Previous to the catalytic tests, the Pt/TiO_2 catalysts was subjected to reduction treatments under flowing H_2. Fig. 1 shows the TEM images corresponding to the Pt/TiO_2 catalyst reduced *ex situ* at 473 K, along with a particle size distribution histogram. The dark spots are due to platinum particles, whereas the lighter parts correspond to titanium dioxide crystallites. The mean sizes of the