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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, $T_{\mathrm{injector}} = 548$ K, $T_{\mathrm{column}} = 333$ 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

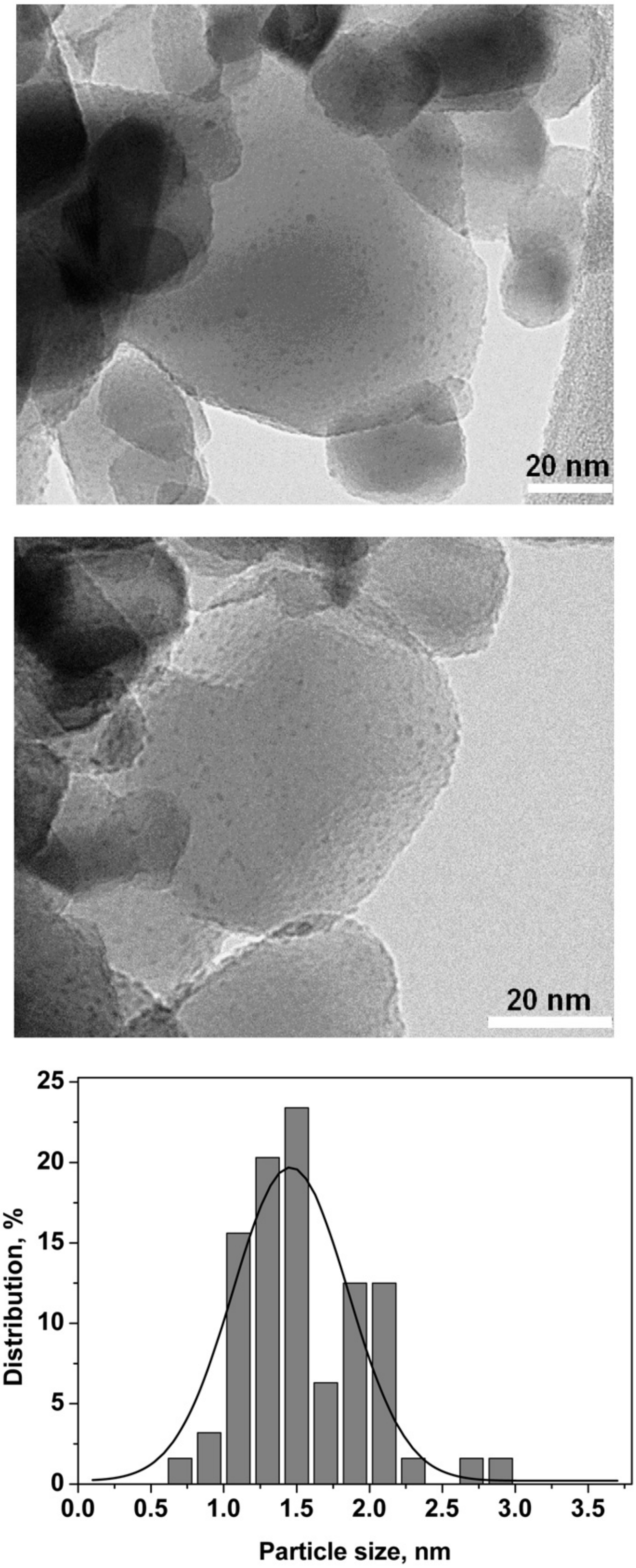


Fig. 1. TEM images and distribution of Pt particle sizes in Pt/TiO$_2$ reduced at 473 K. The sizes were determined for more than 100 nanoparticles selected at random.

main body of the platinum particles are between 1 and 2 nm. The micrographs also clearly show that the particles have a spherical or hemispherical morphology and are well dispersed on the support crystallites.

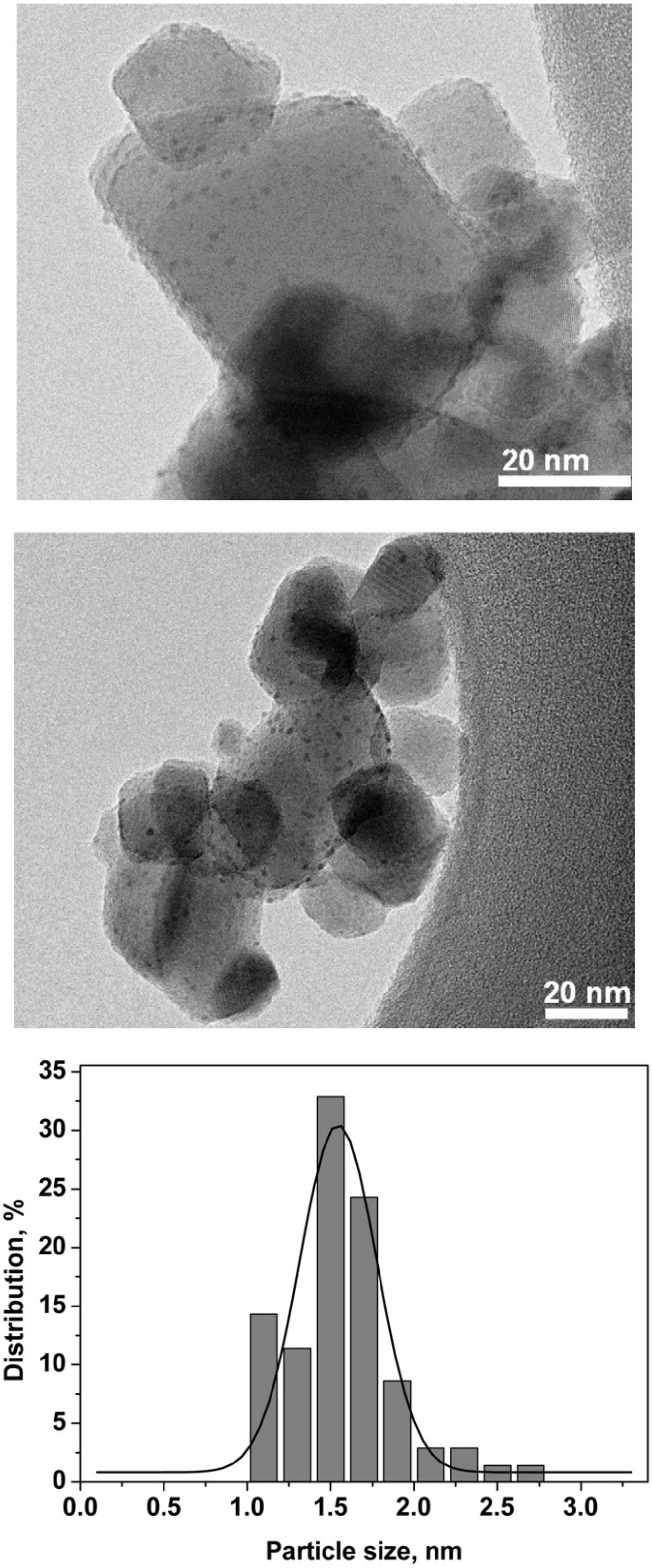


Fig. 2. TEM images and distribution of Pt particle sizes in Pt/TiO$_2$ reduced at 773 K. The sizes were determined for more than 100 nanoparticles selected at random.

No substantial modification of the platinum particles was seen in the catalyst reduced *ex situ* at 773 K (Fig. 2). The particle size distribution profile differs slightly, but the mean particle size remains similar to that of its counterpart reduced at 473 K. Thus, it can be concluded that the increase of the reduction temperature

Table 1
XPS characterization of the Pt/TiO_2 catalysts.

Reduction temperature (K)	Pt $4f_{7/2}$ binding energy (eV)	Pt/Ti, atomic
473	70.9	0.0225
773	70.6	0.0135

Table 2
CO uptake and platinum dispersion for the Pt/TiO_2 catalysts reduced at 473 and 773 K.

Reduction temperature (K)	CO uptake (μmol/g)	Pt dispersion (%)		Pt particle size (nm)	
		CO chem.	TEM	CO chem.	TEM
473	40.5	53	68	2.0	1.6
773	5.0	7	68	15.4	1.6

to 773 K does not produce any sintering of the platinum particles. Unfortunately, the resolution of the TEM system used does not allow discernment of the coverage of the metal particles by patches of partially reduced support.

The chemical composition of the catalyst surface was evaluated by XPS. Table 1 reports the binding energy of the Pt $4f_{7/2}$ level for the catalysts reduced *in situ* under hydrogen at 473 and 773 K for 1 h. A single peak centered at 70.9 and 70.6 eV appeared for the catalysts reduced at low temperature and high temperature, respectively, which is assigned to platinum in the metallic state. The shift to lower binding energy on catalyst reduction at 773 K can be attributed to several factors, such as a lower amount of surface chlorine, the metal–support interaction (SMSI) effect, or larger Pt particles yielded on metal sintering. The TEM results allow the rejection of this latter possibility (i.e., the sintering of platinum particles). On the other hand, the loss of surface chlorine content with increasing reduction temperature has been reported by Huidobro et al. [27] and Silvestre-Albero et al. [40] in earlier studies on Pt/TiO_2, in such a way that the Cl/Ti surface ratio detected by XPS decreased from 0.014 to 0.007 when the reduction temperature was increased from 473 to 773 K. More recently, it has been demonstrated that values shifted slightly to lower binding energies in Pt/TiO_2 catalysts may be indicative of the SMSI effect [41,42].

The surface Pt/Ti atomic ratio can be considered a measurement of the platinum dispersion on the support. This parameter decreased with increasing reduction temperature, thus indicating a loss of surface platinum with increasing reduction temperature. The sintering of metal particles due to the reduction treatment could explain this result, as could the decrease in Pt $4f_{7/2}$ binding energy after reduction at high temperature noted earlier. No metal sintering was observed by TEM analysis, however. Another possible explanation is the SMSI effect, through which reduction at 773 K produces the formation of partially reduced TiO_{2-x} species that migrate and decorate the metal particles, with the covered platinum surface thus partially undetected by the XPS technique.

Manometric CO chemisorption was used to assess the metal dispersion (ratio between surface and total platinum atoms in the catalyst). A CO:Pt = 1:1 adsorption stoichiometry was assumed, and the average particle size was calculated from the dispersion value using the following equation, where P_d is the average diameter of the platinum particles in nm, and D is the metal dispersion:

$$P_d = \frac{1.08}{D}.$$

Table 2 reports the amount of CO adsorbed by the catalyst after the reduction treatments at both low (473 K) and high (773 K) temperatures, along with the platinum dispersion and the average particle sizes. For comparison, values obtained from TEM measurements also are included. After reduction at 473 K, the platinum particle sizes and dispersion values obtained from CO chemisorption and TEM were quite similar; however, the CO uptake strongly decreased after reduction at 773 K, in good agreement with the Pt/Ti XPS atomic ratio trend. The strong loss in CO adsorption capacity (which was <10% of that after reduction at low temperature) reflects the high coverage of platinum particles by partially reduced titania after reduction at high temperature, because TEM results show no enlargement of the metal particles by sintering.

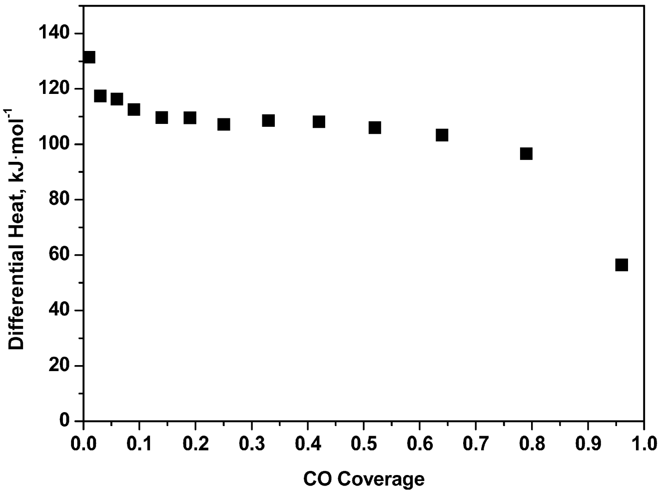


Fig. 3. Differential heats of CO adsorption as a function of the adsorbate coverage at 298 K for the catalyst reduced at 473 K.

The form and strength of CO chemisorption on platinum depend on the surface structure of the particles. Adsorption microcalorimetry can yield information about the energetic interaction of CO with the platinum surface, which provides an indication of its heterogeneity. In this technique, small doses of CO are contacted with the reduced catalyst, and the differential heat of adsorption is measured as a function of CO coverage. On an energetically heterogeneous surface, the most energetic sites are covered first, and thus the differential heat of adsorption decreases continuously with increasing CO adsorption.

Fig. 3 shows the differential heat of CO adsorption at 298 K as a function of the coverage for the catalyst reduced at 473 K. Three main regions can be distinguished. In the first region, the heat of adsorption is 130 $kJ\,mol^{-1}$, which dramatically decreased to 115 $kJ\,mol^{-1}$. In the second region, a plateau with a nearly constant value of 110 $kJ\,mol^{-1}$ was obtained. Finally, in the third region, the heat of adsorption decreased with the coverage up to the physisorption region, where the metal surface was saturated.

After reduction at 773 K, the heat of CO adsorption versus coverage profile (Fig. 4) reveals a slightly lower initial heat of adsorption ($\approx$126 $kJ\,mol^{-1}$). The low CO uptake of this catalyst (5 $\mu mol\,g^{-1}$) complicates the analysis, because only a few doses can be introduced. Thus, describing the tendency with actual precision is difficult. To better compare the results, both curves obtained after different reduction temperatures have been plotted in the same graph. The graph shows how the heat of adsorption was lower than that for the sample reduced at 473 K over the wide range of coverage, except for the low coverage part, where the heat of adsorption was similar or somewhat higher. Given the absence of evidence for sintering, a strong interaction of the platinum particles with the partially reduced titania support is suggested as the cause of the lower heat of adsorption. A modification of the surface morphology after reduction treatment at 773 K also would explain this result. The particles would tend to form a denser structure [43], with sites displaying a higher degree of coordination, for which the heat of CO adsorption would be lower.

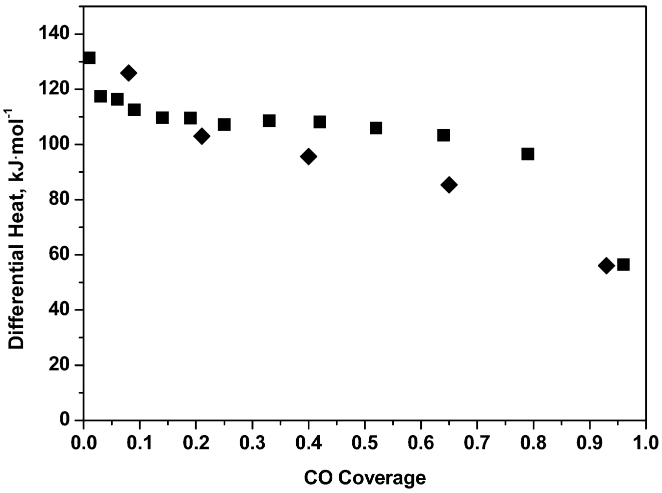


Fig. 4. Differential heats of CO adsorption as a function of the adsorbate coverage at 298 K for the catalyst reduced at 473 K (■) and 773 K (◆).

3.2. *Catalytic activity in the transfer hydrogenation of acetophenone*

Acetophenone was chosen as a model substrate to test the catalytic activity of the titania-supported platinum nanoparticles in the transfer hydrogenation with isopropanol. Two Pt/TiO_2 catalysts were studied, both containing 1.5 wt% Pt and one reduced at 473 K and the other reduced at 773 K (Table 3). The catalyst reduced at 473 K did not show any catalytic activity when the reaction was performed in the absence of base at room temperature (entry 1, Table 3), whereas low conversion was achieved with the same catalyst by heating at 349 K in the absence of base (entry 2, Table 3). The incorporation of KOH into the reaction mixture showed a clear beneficial effect, substantially increasing the yield and reducing the reaction time to only 1 h (entry 3, Table 3). It is well known that conversion of the alcohol into the alkoxide by reaction with a base (isopropanol into potassium isopropoxide in this case) enhances the reactivity toward the hydride donation [4]. The possibility of reusing the catalyst also was studied. Thus, for each cycle, the catalyst was decanted and the supernatant was removed, followed by the addition of more isopropanol, KOH, and acetophenone. The Pt/TiO_2 reduced at 473 K could be reused in a second cycle with no any apparent loss of activity (entry 4, Table 3), whereas the yield dropped significantly in the third cycle (entry 5, Table 3). A similar yield was obtained in the first run when Pt/TiO_2 was reduced at 773 K as when it was reduced at 473 K, with the reaction being faster with the latter (compare entries 3 and 6 in Table 3). But the former catalyst was superior from a reuse standpoint, exhibiting good performance during four consecutive cycles (entries 6–9, Table 3), although a drastic decrease in activity was observed for the fifth run (entry 10, Table 3).

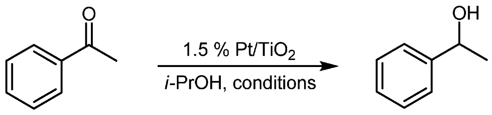
The aforementioned decrease in activity could not be ascribed to partial leaching of platinum from the support, as we confirmed by ICP. In fact, it has been recently reported that the catalytic activity of heterogeneous catalysts based on group 8 metals can be suppressed after aging with alcoholic solvents (8–20 h) as methanol, ethanol, 1-propanol, and 2-propanol [44]. Surface science studies found that in these cases, the alcohol underwent dissociative adsorption on the metal surface to form a metal alkoxide, which decomposed by formation of CO and carbonaceous species. A similar process could account for the deactivation of our Pt/TiO_2 catalysts after several cycles under the reaction conditions.

The different catalytic behavior observed for the catalysts reduced at 473 and 773 K was related to the information obtained from their CO absorption capacity, as noted earlier. Thus, the finding that the reduction at a higher temperature led to Pt particles that interacted strongly and were highly covered with the partially reduced titania support can be associated with the longer reaction time (2 vs 1 h) needed for this catalyst to achieve the same product yield as its counterpart reduced at lower temperature. Furthermore, this shielding effect of the support could lengthen its catalytic life, allowing a larger number of cycles, in agreement with the results observed in the vapor-phase hydrogenation of the carbonyl group catalyzed by Pt/TiO_2 [27–34].

Hydrogen transfer reductions have been little studied from a mechanistic standpoint compared with their homogeneous counterparts. Nevertheless, based on deuteration experiments, it has been demonstrated that under similar conditions as described in this report (5% Pd/C, NaOH, *i*-PrOH, 64 °C), the α-hydrogen of isopropanol is transferred to the substrate through a monohydride-type mechanism [36]. In contrast, a dihydride-type mechanism, involving both the α-hydrogen and hydroxyl group hydrogen, seems to operate in the catalytic system composed of 20% nickel nanoparticles and *i*-PrOH at 76 °C in the absence of any added base [21]. Therefore, a monohydride-type mechanism can be invoked in the case of the hydrogen transfer reduction of acetophenone catalyzed by Pt/TiO_2 described herein.

Finally, it is noteworthy that no byproducts were detected in these experiments using an efficient, reusable, and simple catalytic system composed of Pt/TiO_2, KOH, and isopropanol.

Table 3
Transfer hydrogenation of acetophenone catalyzed by Pt/TiO_2[a].



Entry	Cycle	Catalyst reduction *T* (K)	Base[b]	*T* (K)	*t* (h)	Yield (%)[c]
1	1	473	–	rt	24	0
2	1	473	–	349	24	30
3	1	473	KOH	349	1	87
4	2	473	KOH	349	1	88
5	3	473	KOH	349	24	23
6	1	773	KOH	349	2	86
7	2	773	KOH	349	2	86
8	3	773	KOH	349	2	91
9	4	773	KOH	349	2	76
10	5	773	KOH	349	2	3

[a] All reactions were performed with 100 mg of catalyst (0.0077 mmol Pt, 0.8 mol% Pt referred to acetophenone).
[b] 1 mmol of KOH was used.
[c] GLC yield. No change in yield was observed after the specified reaction time.

4. Conclusion

In this work, platinum nanoparticles supported on titania were synthesized by an impregnation method, followed by reduction at 473 or 773 K and then characterization by TEM, XPS, and microcalorimetry of CO adsorption at room temperature. These titania-supported platinum catalysts were shown to effectively catalyze the hydrogen transfer reduction of acetophenone using isopropanol as the hydrogen donor. To the best of our knowledge, this is the first time that a platinum catalyst has been successfully applied to the transfer hydrogenation of carbonyl compounds with isopropanol, with the reaction proceeding in short reaction times and high yields. Moreover, the catalyst reduced at 773 K could be easily reused and maintained good catalytic activity over four consecutive cycles. Further studies on the application of this methodology to other substrates are underway.

Acknowledgments

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