Restructuring during pretreatment of platinum/alumina for enantioselective hydrogenation

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Received 26 June 1999; accepted 30 September 1999

The influence of reductive and oxidative heat treatment on the enantioselectivity of chirally modified Pt/alumina has been reinvestigated, using the hydrogenation of ketopantolactone as a test reaction. Enhancement in ee by 39–49% has been observed after treatment in hydrogen at 250–600 °C, as compared to untreated or preoxidized catalysts. The changes in ee after reductive and oxidative treatments are reversible, and always the final treatment is decisive. A HRTEM study indicates that adsorbate-induced restructuring of Pt crystallites during hydrogen treatment at elevated temperature can play a role in the selectivity improvement, but the changes are superimposed by the strong structure-directing effect of the alumina support. The possible contribution of other effects (complete reduction of Pt^{n+} surface species, removal of impurities, or change of Pt particle size) could be excluded.

Keywords: enantioselective, hydrogenation, ketopantolactone, cinchonidine, catalyst pretreatment, adsorbate-induced restructuring

1. Introduction

The concerted effort of several research groups in the past two decades led to a substantial improvement in understanding of Orito's reaction [1,2], the enantioselective hydrogenation of α-ketoesters over Pt modified with cinchona alkaloids (see, e.g., [3,4]). Nevertheless, there are still some interesting and important observations which deserve an unambiguous explanation. It was shown early [1,2,5–7] that preheating the catalyst in H_2 has a great influence on the enantiomeric excess (ee). In the most impressive example the ee to (R)-ethyl mandelate increased from 34 to 84% after prereduction of 5 wt% Pt/alumina in H_2 at 400 °C [2]. On the other hand, preheating of Pt/alumina in air or vacuum has no positive effect on the ee in α-ketoester hydrogenation [8].

Orito et al. [2] assumed that the positive effect of reductive pretreatment was due to the removal of oxygen adsorbed on Pt. However, in the hydrogenation of ethyl 2-oxo-4-phenylbutyrate, reoxidation of a Pt/alumina catalyst in ambient air, subsequent to prehydrogenation at 400 °C, diminished the ee only by 2% [9]. Apparently, the oxidation state of Pt at the beginning of the hydrogenation reaction had no influence on the enantioselectivity.

In some studies the positive effect of reductive pretreatment depended on the catalyst support: Pt/alumina was considerably more sensitive to thermal treatment than Pt/SiO_2 and Pt/C [6,9]. However, no feasible explanation for this difference has been provided yet.

Enhancement of enantioselectivity after reductive heat treatment of Pt/alumina is not limited to the hydrogenation of α-ketoesters. Under otherwise identical conditions the ee could be doubled in the hydrogenation of trifluoroacetophenone [10], ketopantolactone (KPL) [11] and some pyrrolidine-triones [12].

It has also been shown that the average particle size of Pt increases during heat treatment in H_2 [11]. This observation corroborates a former proposal [8,13] that small Pt particles (<3–4 nm) are less selective in the hydrogenation of ethyl pyruvate. The metal particle size can influence the distribution of exposed face, edge or corner atoms [14], and hence the adsorption of hydrogen and organic species.

A feasible explanation for the positive effect of H_2 at high temperature could be the role of surface morphology of supported Pt particles. Adsorbate-induced restructuring [15] of Pt during reductive pretreatment may favour the appropriate adsorption of reactant and chiral modifier, and their interaction on the metal surface, in the subsequent hydrogenation reaction. Striking topographic changes were observed by STM when Pt(111) was exposed to H_2, O_2 or CO at 150 °C [16]. The corrosive restructuring of Pt(111) and Pt(110) surfaces, induced by CO adsorption, was detectable already at room temperature [16,17].

The aim of the present work is to investigate possible restructuring of supported Pt particles during pretreatment at elevated temperature and its role in the enantiodifferentiating ability of cinchona-modified Pt. The performance of alumina-supported Pt is tested in the hydrogenation of KPL to the industrially important (R)-pantolactone [18], according to scheme 1.

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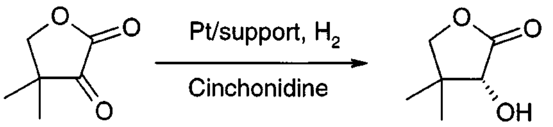

Scheme 1.

2. Experimental

The 40–50 μm fraction of a 5 wt% Pt/alumina (Engelhard 4759) was used for the experiments. Catalyst pretreatment was performed in a fixed-bed reactor by flushing the catalyst with 12.5–30 $cm^3\ min^{-1}$ H_2 (99.999%, <2 ppm O_2, <0.5 ppm C_nH_m), Ar (99.9998%), air (0.033% CO_2) or CO (<3 ppm O_2) for 1.5 h. Reductive and oxidative treatments were separated by flushing with nitrogen (99.995%, <10 ppm O_2) for 0.5 h at the temperature of the next treatment. Finally, the catalyst was cooled to room temperature in the gas flow used in the last pretreatment step, and transferred into the autoclave under exclusion of air. For HRTEM measurements, treatments in H_2 and air were performed at 600 °C also for prolonged time (14.5 h).

Hydrogenation of ketopantolactone (KPL) was carried out in a mechanically stirred 100 cm^3 stainless-steel autoclave (Parr 4560 Mini, $n = 700\ min^{-1}$). Pressure was held at a constant value and hydrogen uptake followed by a computerized constant volume–constant pressure equipment (Büchi BPC 9901). Under standard conditions, 60 mg pretreated catalyst, 2 g (15.6 mmol) KPL, 50 cm^{-3} toluene and 27.2 μmol cinchonidine were used at 70 bar and −9 °C. KPL was dissolved in toluene and dried by azeotropic distillation before each reaction. The reaction was stopped after 2 h, except when the hydrogen consumption ceased earlier. The slurry was diluted with 20 cm^{-3} ethanol and analyzed by a HP 5890A gas chromatograph with a chiral capillary column (WCOT Cyclodextrin-β-2,3,6-M-19, Chrompack). Enantioselectivity is expressed as ee $= R\ (\%) - S\ (\%)$; sd $= \pm 0.5\%$. Initial rate (r_0) was determined from the hydrogen consumption curve by extrapolating to zero time (from the region above 20% conversion). Under standard conditions the rate of hydrogen uptake was independent of the stirrer frequency, but depended on the catalyst particle size. This indicates some pore diffusion limitation, likely due to product crystallization in the pores at the low reaction temperature [19]. Accordingly, the calculated values cannot be considered as intrinsic kinetic rates.

X-ray diffraction patterns were obtained on a Siemens D5000 powder X-ray diffractometer using Cu K_α radiation (Ni filter). The sample was rotated during measurement by 30 rpm. Mean Pt particle size was calculated from the line broadening of the (111) reflection by the Scherrer formula.

XPS measurements were performed with a Leybold Heraeus LHS11 apparatus using Mg K_α radiation. The work function of the spectrometer was set so that the Au $f_{7/2}$ line for metallic gold was located at 84.0 eV. Thin sample films were pressed on a sample holder, evacuated in a load lock, and subsequently transferred into the UHV chamber for analysis. Slight sample charging was corrected using the C 1s line at 284.6 eV as an internal standard. Differential charging was estimated by varying the potential of a tubus in the lens system of the analyzer. The analysis is complicated by the overlapping of the most intensive Pt line (4f) with that of Al 2p [20], and only the Pt $4d_{5/2}$ lines could be used.

Transmission electron microscopy (TEM) was performed using a Philips CM30T electron microscope with a LaB_6 filament as the source of electrons operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in n-hexane on the grid, followed by drying under ambient conditions, all in an Ar glove-box. Samples were transferred to the microscope in a special vacuum-transfer sample holder under exclusion of air. Volume-weighted mean particle size was calculated using the formula: $d = \sum n_i d_i^4 / \sum n_i d_i^3$.

3. Results

3.1. Catalytic hydrogenation

The effect of catalyst heat treatment in different atmospheres on the performance of 5 wt% Pt/alumina in the KPL $\rightarrow$ (R)-pantolactone hydrogenation is illustrated in table 1. Pretreatment in flowing hydrogen enhanced considerably the ee, showing a broad maximum between 250 and 600 °C. After prereduction at 400 °C, TEM and XRD measurements indicated a ca. 30% increase in Pt particle (crystallite) size. The presence of water vapour in hydrogen at 400 °C had practically no influence on the performance of Pt, but the average metal particle size decreased to 2.8 nm, which contrasts the behaviour in the absence of water where the particle size increased to 4.2 nm.

Oxidative treatment in air barely influenced the Pt particle size, the initial rate and enantioselectivity. That is, heat treatment alone of the already oxidized Pt has no positive influence on its performance. This and the former conclusion are in good agreement with our results obtained in ethyl pyruvate hydrogenation [8,13]. Catalysts pretreated in pure Ar or CO afforded medium enantioselectivities. Due to their moderate effect, the influence of these gases will not be discussed further.

Reductive catalyst pretreatment increased also the initial rate of hydrogen consumption. For the interpretation of this change we have to consider that when using an untreated catalyst (stored in air), before hydrogenation of the reactant the surface PtO_x has to be reduced to the active Pt^0 species. This transient period is short or may be completely absent for Pt/alumina prereduced at high temperature, resulting in an apparent higher initial reaction rate. However, the average rates of KPL conversion accounting for the whole reaction were rather similar, almost independent of the pretreatment procedure.

It is interesting to consider the two extreme cases, the heat treatments in hydrogen and air, in more detail. Data

Table 1
Influence of various pretreatment procedures on the catalytic performance of 5 wt% Pt/alumina.

Catalyst pretreatment	Temp. (°C)	d_{TEM}[a] (nm)	d_{XRD}[b] (nm)	r_0 (mmol g^{-1} min^{-1})	Conversion (%)	ee (%)
No treatment	–	3.3	3.1	11	99	46
H_2	100	–	–	13	95	67
H_2	250	–	–	24	80	86
H_2	400	4.2	4.1	32	87	89
H_2	500	–	–	58	97	86
H_2	600	–	–	20	84	85
H_2/H_2O[c]	400	2.8	–	42	87	87
Air	400	3.3	3.2	10	97	46
Air	600	–	–	16	98	40
Air/H_2O[c]	400	–	–	7	99	40
Ar[d]	400	–	–	13	97	68
CO	400	–	–	16	97	57

[a] Volume-weighted mean particle size determined by TEM.
[b] Crystallite size determined by XRD line broadening.
[c] Gas flow saturated with water at room temperature.
[d] Treatment for 2 h.

Table 2
Influence of the sequence of reductive and oxidative pretreatments on the catalytic performance of 5 wt% Pt/alumina.

Catalyst pretreatment (temperature in °C)	r_0 (mmol g^{-1} min^{-1})	Conversion (%)	ee (%)
H_2 (400)–air (400)	14	99	44
Air (400)–H_2 (400)	–[a]	99	87
Air (600)–H_2 (400)	32	69	89
Air (400)–H_2 (400)–air (400)	10	99	45
H_2 (400)–air (400)–H_2 (400)	37	95	89
H_2 (400)–air (25)	20	84	84
Air (400)–H_2 (25)	21	99	57

[a] Not measured.

collected in table 2 demonstrate that the changes during these treatments are reversible. When applying several subsequent reductive–oxidative heat treatments, always the last step in the cycle determined the performance of the catalyst. Treatments at room temperature either in hydrogen or air led only to minor changes.

Interestingly, no difference in the oxidation state of Pt after reductive and oxidative treatments at 400 °C could be detected by XPS analysis. Only Pt^0 was detected, independent of the pretreatment conditions. The likely explanation is that the surface layer of the sample was easily reduced in the load lock due to the reducing conditions (reducing gas in the zeolite trap, hydrogen from the ionization gauge, or pump oil vapor [21]).

3.2. Transmission electron microscopic measurements

The 5 wt% Pt/alumina after various pretreatments has been investigated by HRTEM. Two types of alumina could be distinguished: a properly crystalline and a less crystalline form. (Note that XRD indicated the presence of only γ-Al_2O_3.) The catalyst in an oxidized state (treated in air at 600 °C for 14.5 h) contained predominantly spherical particles on both types of alumina. After a reductive treatment at 600 °C the morphology of Pt particles depended mainly on the crystallinity of the support: mostly faceted (cube-like or hexagonal) on crystalline alumina, whereas rounded shapes dominated on the less crystalline alumina. Corresponding electron micrographs are shown in figure 1. This behavior was less clear after pretreatments under milder conditions.

Besides, TEM confirmed that the shape and size of Pt particles after treatments at 400 °C in pure H_2 or H_2 saturated with water were similar, in agreement with the result of the catalytic study. Similarly, an exposure to ambient air of the sample reduced at high temperature did not influence the morphology of Pt particles.

4. Discussion

The studies corroborate the former observation [11] that catalyst treatment in flowing hydrogen at 400 °C can approximately double the ee to (R)-pantolactone, compared to the performance of untreated or preoxidized Pt. A new observation is that the change in ee after reductive and oxidative treatments is reversible and always the last treatment determines the catalytic performance.

There are several possible reasons for the improved enantiodifferentiation after reductive heat treatment of Pt:

(i) cleaning of the surface from impurities,
(ii) increase of Pt particle size,
(iii) complete reduction of Pt^{n+} at high temperature, and
(iv) special surface geometry of hydrogen-treated Pt particles.

Surface impurities can certainly play a role in many instances and reductive removal of some strongly adsorbed species (e.g., residues from precursor) can contribute to the observed effect. Thermal analysis (TG and DTA combined with MS) and XPS did not show the presence of any impurity in significant amount in the Pt/alumina catalyst. Also the reversible changes observed after reductive and

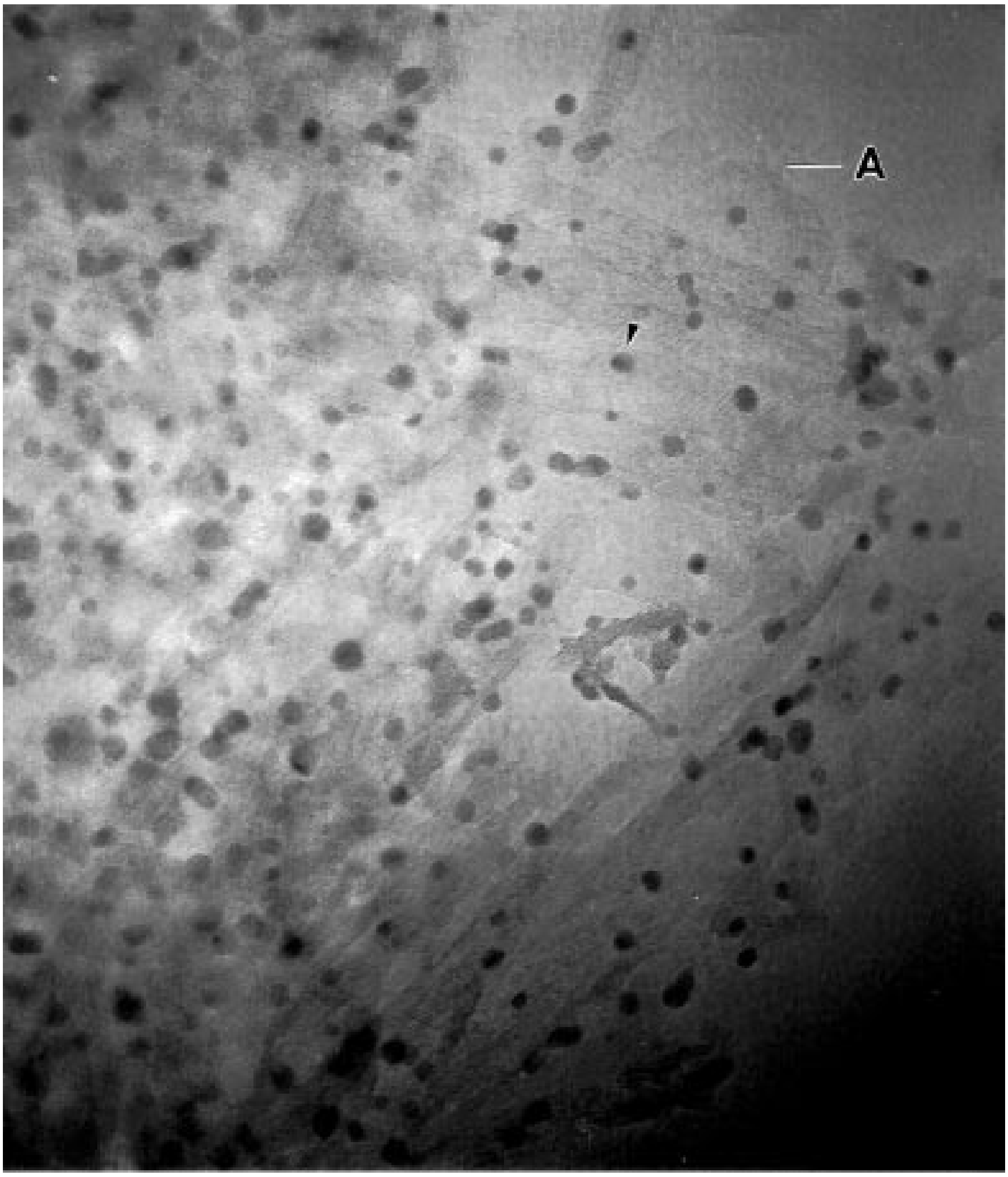

Figure 1. High-resolution transmission electron micrographs of the 5 wt% Pt/alumina catalyst after treatment at 600 °C (same magnification, scaling bar: 7.5 nm). (A) Air-treated sample showing mainly spherical metal particles irrespective of the local morphology of alumina; (B) hydrogen-treated sample showing both faceted and spherical particles mainly present on the properly crystalline parts of alumina.

oxidative heat treatments (table 2) suggest that the effect of impurities is negligible.

The similar behaviour of Pt/alumina irrespective of the particle size ($d_{\mathrm{av}} = 2.8$ or 4.2 nm), established after prereduction in dry or humid hydrogen (table 1), indicates that the size of Pt particles in this range does not significantly influence the enantiodifferentiating step.

The influence of the oxidation state of Pt before and during enantioselective hydrogenation has been the target of previous research, leading to contradictory conclusions [2,8,9,22,23]. Incomplete reduction of supported Pt particles at room temperature could be a feasible explanation for the positive effect of high-temperature catalyst prereduction (table 1). It was shown by TPR experiments that complete reduction by hydrogen of surface PtO_2 and $PtAl_2O_4$ species on a Pt/alumina catalyst required minimum 100–220 °C, and the reduction behavior was a function of metal dispersion and preoxidation conditions [24]. Also XPS analysis of a series of 1.4–10 wt% Pt/alumina showed that at least 150 °C was necessary for complete reduction to metallic Pt, and the lower the metal loading, the higher was the minimum reduction temperature [20]. However, the use of Cl-containing Pt precursors for catalyst preparation in the above two studies can seriously distort the results. The high surface Cl concentration during catalyst reduction [25] can stabilize the oxidized state of Pt and hinder its facile reduction at ambient temperature. Besides, the explanation by Hwang and Yeh [24] seems to be rather

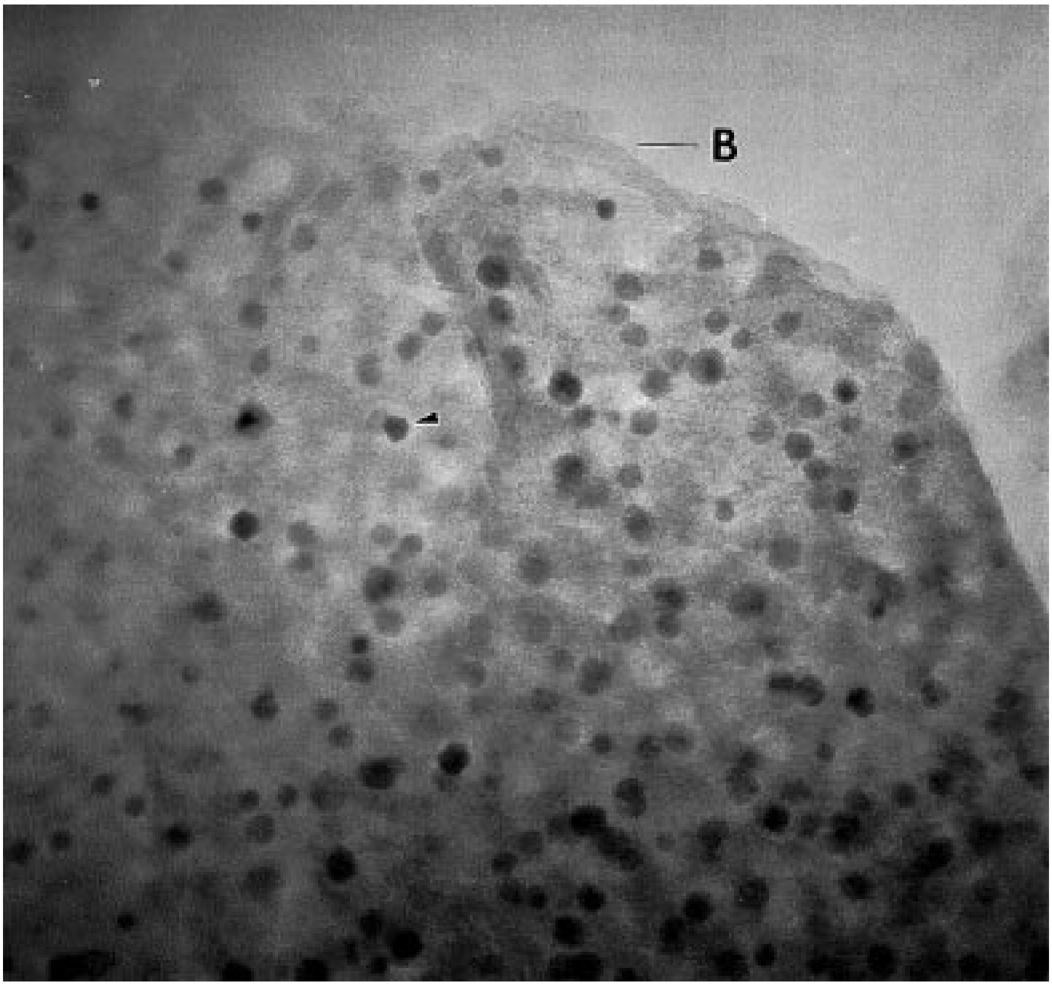

Figure 1. (Continued.)

speculative as there is no evidence in the open literature for the existence of $PtAl_2O_4$.

We have found by XPS that even after an oxidative treatment the 5 wt% Pt/alumina was easily reduced at room temperature. Accordingly, we propose that in our case the presence of unreduced surface Pt^{n+} species cannot play an important role in the enantioselective hydrogenation of KPL.

There is no doubt that adsorbates such as H_2, O_2 or CO can induce dramatic surface restructuring of Pt already at 150 °C [15–17]. Supported Pt requires higher temperature for the transformation and at ambient temperature it can exist indefinitely in this metastable configuration [26]. Heating at 450–625 °C of 2–20 nm Pt particles supported on silica or alumina afforded cube-like shapes with facets in hydrogen and spherical particles in air or N_2 [26,27]. The changes in particle shape monitored by TEM were reversible. Restructuring during annealing could be modelled by simple first-order calculations, based on the different adsorption energies of hydrogen on Pt(100), Pt(110) and Pt(111) faces [27]. Reversibility of substrate-induced restructuring and the rounded shape after annealing in air has been confirmed later, but spherical shape for <5 nm particles and near-cubooctahedral shape for larger particles were observed in H_2 [28]. The discrepancy was partly attributed to surface contaminants of support materials, but Pt precursors containing Cl ions or organic ligands could also contribute to the absence of restructuring of small Pt particles.

Our HRTEM investigations indicate that the morphology of Pt particles is related to both the morphology of the alumina support and the pretreatment procedure. The expected faceted Pt particles after reductive heat treatment could be observed only on properly crystalline γ-alumina, while rounded shape was typical for Pt particles located on less crystalline γ-alumina regions, indicating that the alumina support has some structure-directing influence. In order to arrive at a final conclusion concerning the relevance of adsorbate-induced restructuring during pretreatment, the present studies have to be extended to specially designed model systems which allow the structure-directing influence of the support material to be ruled out.

5. Conclusions

There are several important parameters which can influence the behaviour of Pt-catalyzed enantioselective hydrogenation of activated ketones. Catalyst pretreatment in hydrogen at elevated temperature (200–600 °C) belongs to the most influential parameters, which procedure can double the efficiency of cinchonidine-modified supported Pt catalysts. Several assumptions have been considered for the interpretation of this puzzling effect, including the removal of surface contamination, increased particle size, complete reduction of Pt^{n+} surface species, and the adsorbate-induced surface restructuring. Our catalytic, TEM, XPS, XRD and CO chemisorption experiments with Pt/alumina suggest that surface restructuring may be a feasible explanation but an unambiguous interpretation of the dramatic changes in enantioselectivity after reductive and oxidative heat treatments, and the excellent reversibility of these variations, requires further research.

Acknowledgement

XPS analysis by T. Bürgi and XRD measurements by M. Maciejewski, and the financial support by the Swiss National Science Foundation and NWO (The Netherlands) are kindly acknowledged.

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