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Enantioselective hydrogenation of carbonyl compounds over Pd–Pt / alumina catalysts

T. Mallat, S. Szabó, M. Schürch, U.W. Göbel and A. Baiker

Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zurich, Switzerland

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A series of Pd–Pt/alumina catalysts were prepared by consecutive deposition of Pd onto supported Pt particles. Electrochemical model studies indicated that under very mild conditions in aqueous acetic acid the reduction of Pd^{2+} ions occurred partly via the ionization of hydrogen adsorbed on Pt and partly by the slow oxidation of acetic acid. There was only a moderate change in the surface Pd/Pt atomic ratio during heat treatment in flowing hydrogen at 400°C, as determined by XPS analysis. The catalytic performance of the bimetallic catalysts was tested in the enantioselective hydrogenation of ethyl pyruvate and ketopantolactone, in the presence of cinchonidine. Pd was virtually inactive and acted as a site blocker, which decreased the size of Pt ensembles and hindered the formation of the bulky transition complex between the reactant and the chiral modifier. The intrinsically low activity and selectivity of Pd are discussed in the light of H / D exchange studies in deuterated ethanol.

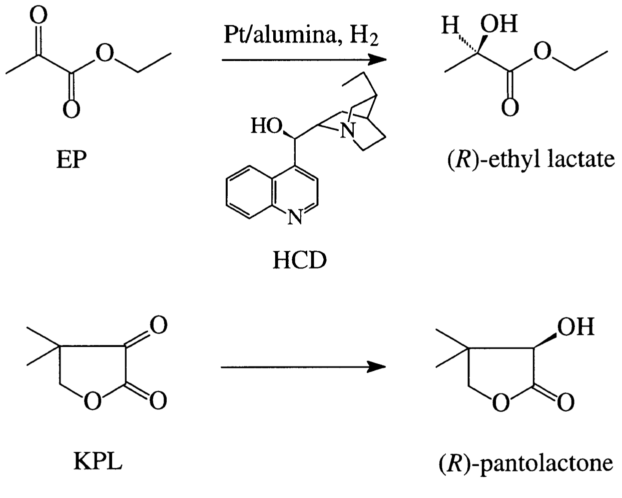
Keywords: preparation of Pd–Pt / alumina, enantioselective hydrogenation, ethyl pyruvate, ketopantolactone

1. Introduction

The enantioselective hydrogenation of activated carbonyl compounds, such as α-ketoesters [1–8], α-ketoacids [9], α,β-diketones [10], ketopantolactone [11] and trifluoroacetophenone [12], has received growing attention in the past years. The most efficient catalyst system is Pt chirally modified with cinchona alkaloids. Interestingly, Pt is far more enantioselective in the presence of cinchonidine (CD), cinchonine, naphthyl ethylamine or dihydrovinpocetin than other metals, which are generally active and chemoselective in the hydrogenation of carbonyl compounds [5,9,13–17]. An example is the hydrogenation of pyruvate esters, in which reaction Pt / alumina modified with simple derivatives of CD afforded 92–95% ee to (R)-lactate in a fast reaction [18]. In contrast, CD-modified Pd was hardly active and provided only 4–5% ee to (S)-lactate [9,13]. There is no unambiguous explanation yet for this behaviour of Pt metals.

Intrigued by the striking differences in the performance of Pt and Pd, we prepared a series of catalysts containing both metals, and tested their enantiodifferentiating ability in the hydrogenation of ethyl pyruvate (EP) and ketopantolactone (KPL, scheme 1). It has been shown earlier that the hydrogenation activity and chemoselectivity of Pd–Pt bimetallic catalysts depends on the surface composition and metal dispersion [19–21]. Both characteristics are strongly influenced by the preparation method and nature of catalyst pretreatment applied before the reaction [22]. A positive, synergic effect on the reaction rate was observed in the hydrogenation of styrene [19]. In contrast, reduced activity of the bimetallic catalysts compared to the more active component was observed in the hydrogenation of 1,3-cyclooctadiene [21] and benzene [23]. Besides, Pd was found to be more selective than any of the bimetallic catalysts in the partial hydrogenation of phenylacetylene, 1,3-cyclooctadiene, 1-octyne and butadiene to the corresponding olefins [19–21,24].

Several methods have been proposed for the preparation of Pt–Pd bimetallic catalysts. The two metals form solid solutions [25], accordingly no special difficulties in the preparation of alloy catalysts are expected. In the generally applied techniques the precursors are introduced simultaneously onto the support followed by their reduction. The success of forming



Scheme 1.

bimetallic particles depends on the relative rate of the deposition and reduction of the two components. In order to avoid this uncertainty, we applied the subsequent selective deposition of Pd onto supported Pt particles. A special technique [22,26,27] was used, by which the reduction of Pd^{2+} ions took place only on the surface of Pt particles.

2. Experimental

Distilled and ion-exchanged water, or triple-distilled and oxygen-free water (for catalyst preparation and electrochemical studies), and analytical grade reagents were used. Dihydrocinchonidine (HCD) was prepared by hydrogenation of CD over Pd/C at 1 bar in a mixture of ethanol–aqueous HCl.

2.1. Catalyst preparation

A 5 wt% Pt/alumina catalyst (Engelhard 4759) was used for preparing a series of bimetallic catalysts. The metal dispersion before and after heat treatment in flowing hydrogen was 0.38 and 0.27, respectively, as calculated from TEM images [28]. The BET surface area of the catalyst was $125\ m^2\ g^{-1}$.

Before Pd deposition, 7 g 5 wt% Pt/alumina was flushed with hydrogen for 1 h in a glass reactor. 50 ml 1 M aqueous AcOH saturated with hydrogen was added and hydrogen was bubbled through the mixture for 2 h. After removal of excess hydrogen by nitrogen (2 h), the proper amount of $Pd(OAc)_2$ in 50 ml 1 M oxygen-free AcOH was added and metal deposition was completed in 16 h under nitrogen. The catalyst was washed with 1 M AcOH then with water to neutral, and dried under an infrared lamp in oxygen-free nitrogen.

2.2. Catalytic hydrogenation

Hydrogenations were performed in a 100 ml stainless steel autoclave with magnetic stirring ($n = 1000\ min^{-1}$). A 50 ml glass liner with a PTFE cap and stirrer were used to keep the system inert. The pressure was hold at a constant value by a computerized constant volume–constant pressure equipment (Büchi BPC 9901). The catalyst was prereduced in flowing H_2 for 1.5 h at 400°C, cooled to room temperature in H_2 and transferred to the reactor with the exclusion of air. Due to the rate enhancement at the beginning of the reaction [6], the average rate of EP conversion was calculated between 10 and 70% conversion on the basis of hydrogen consumption. The enantiomeric excess (ee) at full conversion was determined by an HP 5890A gas chromatograph with a WCOT Cyclodextrin-β-2,3,6-M-19 (Chrompack) capillary column. The enantioselectivity is expressed as ee $(\%) = 100 \times ([R] - [S])/([R] + [S])$.

2.3. X-ray photoelectron spectroscopy (XPS)

The samples were prepared by pressing the catalyst onto adhesive tape normally used for electron microscopy. The spectra were recorded with a Leybold-Heraeus LHS 11 instrument using Mg Kα (1253.6 eV) radiation. The base pressure of the apparatus was lower than 5×10^{-10} mbar. The hemispherical analyzer was operated at a constant pass energy of 38 eV, the energy resolution being 0.9 eV (Ag $3d_{5/2}$). The energy scale was calibrated using Au $4f_{7/2} = 84.0$ eV. Corrections of the energy shift, due to the steady-state charging effect, were accomplished by assuming the C ls line of the adsorbed hydrocarbons as lying at 285.0 eV.

The Pd $3d_{5/2}$ signal and the Pt $4d_{5/2}$ signal were used to calculate the concentrations near the surface. Due to the overlap of these signals, deconvolution of the peaks was necessary. The fitting function used was a mixed lorentzian/gaussian function with a Lorentz/Gauss ratio of 0.9. The FWHM of the corresponding peaks (Pd $3d_{5/2}$,$3d_{3/2}$ and Pt $4d_{5/2}$,$4d_{3/2}$) were set to constant values, which were 3 eV in the case of the Pd peaks and 6 eV for the Pt peaks. For the ΔE of the corresponding peaks induced by spin–orbit coupling a constant value was assumed, which was 5.25 eV for the Pd peaks [29] and 16.8 eV for the Pt peaks [30]. Peak deconvolution led to $d_{5/2}/d_{3/2}$ intensity ratios of 1.5 ± 0.1. This value is in good agreement with that expected for spin–orbit coupling of 3d electrons $(2J + 1)$ [31].

2.4. Electrochemical polarization

Pd deposition onto Pt via ionization of preadsorbed hydrogen was studied in 50 ml 1 M aqueous AcOH containing 10 mg $Pd(OAc)_2$. The experiments were performed under strictly oxygen-free conditions, including the change of electrolyte between polarizations. The method and the electrochemical cell have been described elsewhere [26,32]. The apparent surface area of the platinized Pt working electrode was about 2 cm^2. The reference electrode was a Pt/H_2 electrode in the same supporting electrolyte used in the cell. Continuous bubbling of purified N_2 through the main compartment of the cell deoxygenated and mixed the solution, and removed the traces of H_2 dissolved in the electrolyte during saturation of the working electrode with H_2. All potentials are referred to RHE.

3. Results

3.1. Preparation of the bimetallic catalysts: an electrochemical model study

A special technique, the selective deposition of Pd onto the surface of supported Pt particles was applied for the preparation of alumina-supported bimetallic catalysts. The reduction process was designed to proceed via the ionization of hydrogen preadsorbed on the Pt/alumina catalyst. Preliminary studies indicated that the amount of metal deposited from $Pd(OAc)_2$ in aqueous acetic acid surpassed the theoretical value, assuming a H_{ad} to surface metal atom ratio of 1 to 1 [33]:

$$2H_{ad} + Pd^{2+} \rightarrow Pd + 2H^{+} \tag{1}$$

In order to obtain some insight into the processes taking place during Pd deposition, an electrochemical model study was performed. Pd deposition was studied under conditions very similar to those of catalyst preparation, but the Pt/alumina catalyst was modelled with a platinized Pt electrode due to the conductivity requirements of the electrochemical polarization method.

The most important constant current polarization curves ("charging curves") are collected in figure 1. Curve a, measured in deoxygenated 1 M AcOH, represents the anodic charging curve of platinized Pt used as a reference. Before Pd deposition the potential was decreased to 0.04 V (mimicking the reduction of Pt with hydrogen), then under open circuit conditions 10 mg $Pd(OAc)_2$ was introduced in the 50 ml 1 M AcOH solution. After 20 h equilibration time [26,32] the charging curve of the Pd-covered Pt electrode was measured in pure 1 M AcOH (curve b). The hydrogen region (0.04–0.3 V) of curve b is more than two times longer than that of curve a, i.e. the amount of hydrogen adsorbed on the bimetallic electrode is considerably higher than that adsorbed on the Pd-free Pt surface [26]. Accepting that 1 surface Pt or Pd atom adsorbs 1 H atom [33], curve b indicates that more Pd was deposited than expected from the amount of hydrogen preadsorbed on Pt. (The initial part of curve b runs at about 0.06–0.07 V which corresponds to the $\beta \rightarrow \alpha$ phase transfer of Pd saturated with hydrogen, indicating also some multilayer Pd deposition.)

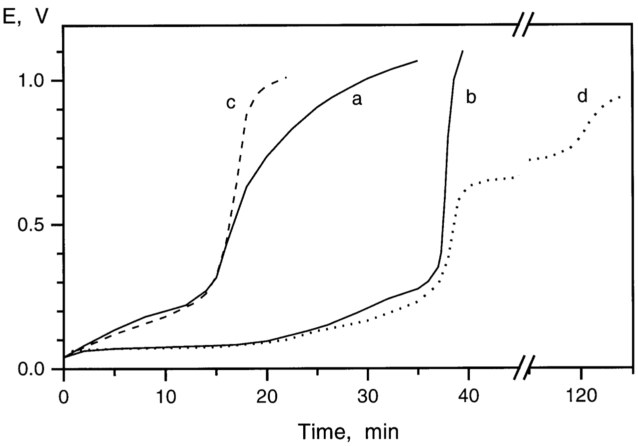


Figure 1. Constant current polarization curves of a platinized Pt electrode in 1 M AcOH (a) and 0.5 M H_2SO_4 (c); and the polarization curves after Pd deposition, measured in 1 M AcOH (b) and 1 M HCl (d); $I = 0.2$ mA, starting potential: 0.04 V.

The amount of Pd deposited was determined by oxidation in aqueous HCl solution:

$$Pd + 4Cl^{-} \rightleftharpoons PdCl_4^{2-} + 2e^{-} \tag{2}$$

The long wave on the polarization curve of the Pd-covered Pt electrode in 1 M HCl between 40 and 120 min at around 0.7 V (figure 1, curve d) corresponds to the oxidation of Pd [26]. On the basis of eq. (2), the amount of Pd was estimated to be five times higher than the "theoretical value", calculated by assuming that Pd^{2+} ions are reduced solely by hydrogen preadsorbed on the Pt surface.

The only possible explanation for this discrepancy is that AcOH, being present during metal deposition, acts as a (weak) reducing agent. This assumption is supported by the deviation between the charging curves of Pt measured in 1 M AcOH and 0.5 M H_2SO_4 (figure 1, curves a and c, respectively). The significant deviation of the two curves above 0.3 V displays the charge (time × current) necessary for the catalytic oxidation of AcOH. Note the potential of Pt during Pd deposition was between 0.04 V (initial value) and 0.58 V (final value) under open circuit and oxygen-free conditions. A further support to our assumption is provided by a recent paper on the oxidation of organic compounds in aqueous solution [34]. It has been shown that the oxidation of AcOH is catalyzed by Pt, but the reaction is extremely slow.

Finally, we have to emphasize an important feature of Pd deposition onto alumina-supported Pt. The metal particles on the non-conductive support act as small metal islands. Pd^{2+} ions are reduced on the Pt surface via the oxidation of adsorbed H or AcOH. Pd^{2+} ions adsorbed on the support remain unchanged. In contrast, when using a conductive support (such as carbon), the oxidation of H or AcOH on the Pt surface and the deposition of Pd on the support could be locally separated and the selectivity of Pd deposition onto Pt would be diminished.

3.2. X-ray photoelectron spectroscopic analysis

The overall (bulk) Pd/Pt atomic ratio of the Pd–Pt/alumina catalysts was varied between 0.012 and 0.25. The surface Pd/Pt atomic ratios, measured by XPS and shown in figure 2, are higher than the bulk ratios due to the preparation technique applied (consecutive deposition of Pd onto Pt). There is a significant change in the surface Pd/Pt ratio after heat treatment in flowing hydrogen at 400°C, which is an important preconditioning step in order to improve the enantioselectivity of the catalyst [1]. The changes represented in figure 2 cannot be simply interpreted as a surface enrichment of Pt in the bimetallic particles. During heat treatment in flowing hydrogen a substantial restructuring of the metal particles occurs. An increase of the average metal particle size by about 40% was shown by TEM [11]. A decrease of

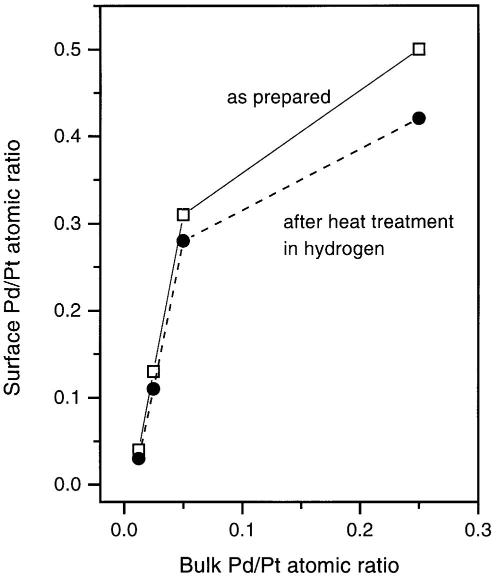


Figure 2. Surface Pd/Pt atomic ratio determined by XPS, as a function of bulk Pd/Pt atomic ratio in the Pd–Pt/alumina catalysts.

metal dispersion is also evidenced by the reduced surface Pt/Al atomic ratios after reductive heat treatment, as illustrated in figure 3.

The change of the Pt/Al ratio with the surface Pt/Pd ratio (figure 3, as prepared catalysts) provides some additional information on the geometry of Pd deposition. After depositing a small amount of Pd (Pd/Pt = 0.04) the Pt/Al ratio decreased significantly, indicating that Pd was deposited mainly as adatoms. At higher Pd/Pt ratio the efficiency of covering the surface Pt atoms by Pd decreases evidencing an increasing proportion of multilayer Pd deposition. For comparison, 65 Pd atoms were deposited onto each 100 surface Pt atoms in case of the catalyst possessing the highest Pd/Pt ratio. It has been shown earlier [26] that one adsorbed Pd atom occupies about 1.5 surface Pt atom. As a consequence, theoretically all the Pd atoms could have been deposited onto Pt as adatoms (monolayer), if the multilayer deposition had not been kinetically favoured [27].

It was also attempted to modify the alumina-supported Pt only with Pd adatoms, avoiding multilayer metal deposition. It has been reported earlier [26] that in aqueous HCl in the presence of excess Pd^{2+} ($PdCl_4^{2-}$) multilayer deposition restructures to adsorbed Pd via ionization and redeposition. Unfortunately, the Pd–Pt/alumina catalysts prepared by this method possessed very poor performance in the hydrogenation reactions, as will be discussed later. XPS analysis revealed that the Al 2s line was shifted from 119.2 eV [35] to 119.6 eV when the catalyst was prepared in the presence of HCl, instead of AcOH. This shift is an indication of the formation of AlO_xCl_y species; the shift is clearly smaller than the difference observed between Al_2O_3 and $AlCl_3$ (0.9 eV [36]). The presence of chlorine in the catalyst was also evidenced by the Cl 2p line at 199.4 eV.

3.3. *Enantioselective hydrogenation reactions*

The bimetallic catalysts were tested in the enantioselective hydrogenation of EP and KPL (scheme 1), and the corresponding results are summarized in figures 4 and 5. A partial coverage of the surface Pt atoms by Pd diminished the rate of EP hydrogenation, but the ee

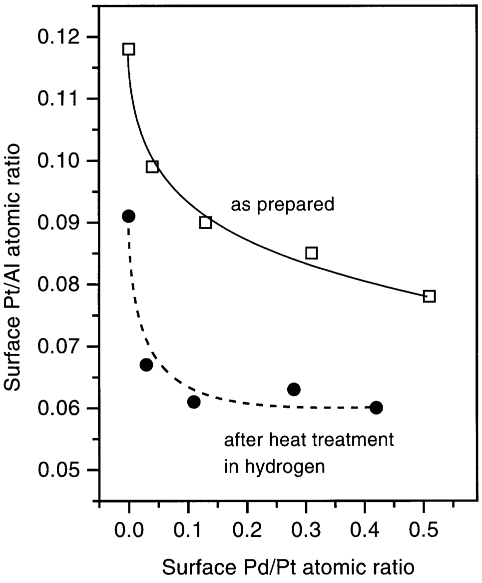


Figure 3. Effect of reductive heat treatment on the correlation between surface Pt/Al and Pd/Pt atomic ratios.

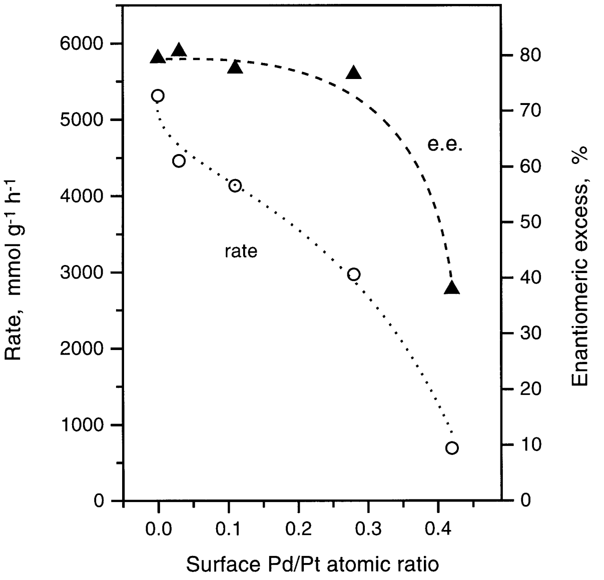


Figure 4. Influence of surface Pd/Pt atomic ratio on the rate and enantioselectivity of EP hydrogenation over Pd–Pt/alumina (conditions: 100 mg catalyst, 15 mg HCD, 10 ml EP, 20 ml toluene, 60 bar, 20°C).

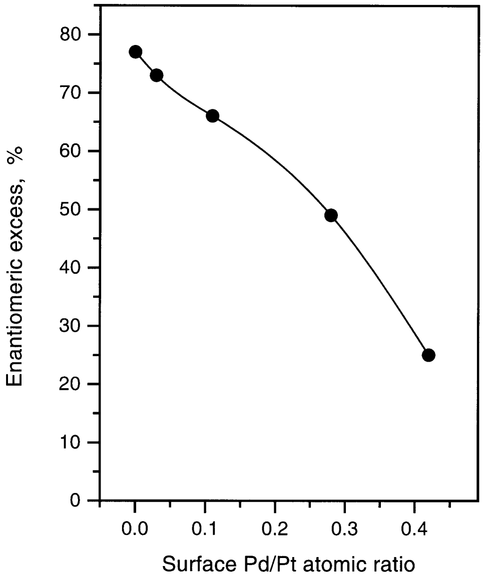


Figure 5. Influence of surface Pd/Pt atomic ratio on the enantioselectivity of KPL hydrogenation over Pd–Pt/alumina (conditions: 150 mg catalyst, 20 mg HCD, 0.5 g KPL, 20 ml toluene, 70 bar, 12°C).

remained almost unchanged till a Pd/Pt atomic ratio of 0.3. The enantioselection in the reduction of KPL is seemingly more sensitive to the substitution of Pt by Pd. Unfortunately, the amount of KPL was too small for an unambiguous determination of the reaction rate on the basis of hydrogen consumption. A common feature of both reactions is that there is no benificial effect of alloying at any Pd/Pt ratios.

Interestingly, a Pd–Pt/alumina catalyst, prepared in aqueous HCl medium (instead of AcOH) and possessing a surface Pd/Pt atomic ratio of 0.32, provided no enantioselection in the hydrogenation of EP. Besides, the reaction rate was very low, considerably smaller than that of the unmodified reaction. The likely explanation is the poisoning of Pt during Pd deposition in the strongly acidic medium where the support is not stable. The presence of AlO_xCl_y type species on the bimetallic catalyst has been evidenced by XPS analysis (see above).

4. Discussion

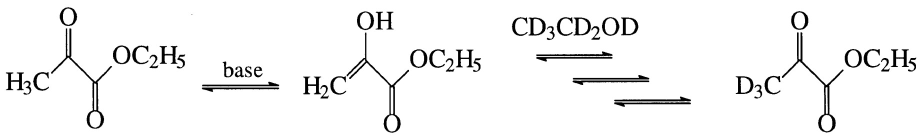
The catalytic experiments, combined with XPS and electrochemical studies, showed that a partial substitution of the surface Pt atoms of a Pt/alumina catalyst by Pd had a strong negative effect in the enantioselective hydrogenation of EP and KPL (scheme 1). In the hydrogenation of EP Pd acted as an inactive species, and covering about one third of the Pt atoms resulted in a loss of activity by almost 90%. This behaviour is even more striking when considering that Pd catalysts are frequently the choice for carbonyl reductions.

It has been proposed earlier [8,37] that the feasible transition complex between CD and EP can adsorb parallel to a flat Pt surface, involving about 20 surface Pt atoms. The size of the active site ensemble and the very low activity and selectivity of Pd in this reaction can explain the detrimental effect of Pd on the performance of Pt. The enantioselective hydrogenation of KPL was even more sensitive to a decrease in the ensemble size of uncovered surface Pt atoms. It seems that the modified reaction is hindered and the (considerably slower) racemic reaction is favoured on the bimetallic catalysts.

The fundamental question: why does Pd act as a virtually inactive species in the enantioselective hydrogenation of carbonyl compounds activated by an electron-withdrawing group in α-position, has not been answered yet. On the basis of H/D exchange experiments, it has been proposed that the poor performance of the Pd/CD system in α-ketoester hydrogenation is due to the exceptional activity of Pd for the saturation of the quinoline rings of CD [2]. However, CD-modified Pd is the most active and enantioselective catalyst for the hydrogenation of α-β unsaturated carboxylic acids [38,39]. In the hydrogenation of 2-methyl-2-pentenoic acid the highest ee was obtained at pressures above 60 bar, without any indication on the saturation of the quinoline rings of CD.

The unexpected behaviour of Pd and the minor excess to (S)-lactate in the presence of CD has been explained recently by the hydrogenation of the enol form of pyruvate which could be formed via dissociative adsorption of the pyruvate molecule [40]. The key evidence to this mechanism was the exchange of H for D in the methyl group of pyruvate, which reaction was observed only on Pd but not on Pt.

In control experiments we found that the H/D exchange via the enolization of EP is rather fast in deuterated ethanol, even in the absence of Pd. In a solution containing 10 μl EP in 0.6 ml deuterated ethanol, 8% of the methyl groups were completely deuterated in 4 h according to scheme 2. Addition of 1 mg CD had a strong catalytic effect on the reaction and the $-CD_3$/



Scheme 2.

–CH_3 ratio was higher than 99 within less than 1 h. Despite the rapid H–D exchange, the actual enol concentration was below the detection limit. (Other reactions between deuterated ethanol and EP, such as transesterification and ketalization [5], are not discussed here.) When 1 μl AcOH was added instead of CD, there was no detectable H/D exchange even after 4 h. These experiments strongly suggest that: (i) the rapid enolization of EP during catalytic hydrogenation should be attributed to base catalysis by the quinuclidine N-atom of CD (or any basic impurity in the catalyst), rather than to the presence of Pd; and (ii) the enolization of EP is not a likely explanation for the low activity and selectivity of Pd when the reaction is performed in AcOH as solvent.

5. Conclusions

The influence of Pd on the catalytic performance of Pt in enantioselective hydrogenation reactions was studied using a series of Pd–Pt/alumina catalysts. Electrochemical model studies demonstrated that not only adsorbed hydrogen, but also the AcOH solvent acted as a reducing agent during the consecutive deposition of Pd onto the supported Pt particles. This astonishing new observation that AcOH can act as a (weak) reducing agent under very mild conditions (1 bar, room temperature) should be taken into consideration when interpreting catalytic hydrogenation reactions over Pt catalysts in acetic acidic medium.

The performance of the bimetallic catalysts was studied in the enantioselective hydrogenation of ethyl pyruvate and ketopantolactone using cinchonidine as the source of chiral recognition. A partial substitution of the surface Pt atoms by Pd, as evidenced by XPS, diminished both rate and ee without any benificial effect at low Pd/Pt ratios. Pd acted as an inert species on the Pt surface and the loss in activity and selectivity is explained by an ensemble effect.

The appropriate interaction of adsorbed reactant and modifier on the metal surface is crucial for enantiodifferentiation. The different adsorption behaviour on Pt and Pd is suggested to be the origin for the strikingly different rates and enantioselectivities observed in the reduction of carbonyl and olefinic compounds catalyzed by these metals. A substantial further step in clarifying the mechanism of the enantioselective hydrogenation reactions will require the study of the simultaneous adsorption of reactant and modifier on the noble metals.

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