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Examination of catalytic behavior and origin of the initial transient period for Pt nanoclusters modified with cinchonidine

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Nanoclusters prepared by a novel water-free method are compared directly with nanoclusters prepared by the known aqueous preparation as well as conventional Pt/Al_2O_3 for the enantioselective hydrogenation of ethyl pyruvate. The catalytic behavior of cinchonidine on colloidal Pt was investigated during ethyl pyruvate hydrogenation in acetic acid under 10 bar of hydrogen at 22 °C with (1 mmol L^{-1}) and without addition of free cinchonidine. The effect of hydrogen pressure, cinchonidine concentration, ethyl pyruvate and catalyst loading on the enantiomeric excess (EE) with time were also studied. Through these studies, we propose that the nature of the observed initial transient period (ITP) for these "quasi-homogeneous" systems may be explained by desorption of the weakly adsorbed tilted "N lone pair bonded" cinchonidine species from the Pt surface due to interaction with hydrogen.

KEY WORDS: cinchonidine; initial transient period; enantioselective hydrogenation; ethyl pyruvate; platinum; nanoclusters; desorption.

1. Introduction

Since the first report of Orito [1], cinchonidine adsorbed on platinum has become a well-known system for asymmetric hydrogenation of α-ketoesters. The initial transient period (ITP) for the Pt/Al_2O_3 system has been reported and investigated by numerous groups and has been the subject of intense discussions [2,3]. ITP was observed by Baiker and co-workers [4] and was attributed to an impurity effect (from destructive adsorption of EP and alcoholic solvents on Pt) which could be eliminated by pre-activation with hydrogen. Blackmond and co-workers proposed the "reaction-driven equilibration" explanation [5] and demonstrated the significant influence of mass transport (gas–liquid diffusion of hydrogen) limitation on the enantioselectivity [6]. Recently, it was shown that ITP is not only the effect of impurities (lactates in ethyl pyruvate) but could also be a result of competitive adsorption of reactant, modifier and solvent [7]. The nature of the effect is still not well understood [8], whereas its understanding might be useful in developing a catalyst which induces constant high enantiomeric excess during reaction, at low hydrogen pressure. In general, ITP is studied with catalyst systems in which the catalyst is modified with cinchonidine *in situ* as opposed to systems in which the catalyst surface is modified with cinchonidine prior to introduction to the reaction vessel. The latter of these catalyst systems allows isolation and characterization of the catalytic species (in the form of a powder) and study of the catalyst/modifier interaction independent of the influence of additional reaction conditions and thus such studies can provide valuable information regarding these very interesting catalysts. Such studies are however limited [9].

Here, we investigate the behavior of enantiomeric excess (EE) during hydrogenation of ethyl pyruvate with commercial Pt/Al_2O_3 and with cinchonidine Pt nanoclusters prepared by two different methods, an aqueous (first reported by Bönnemann [10]) and a novel organometallic method through decomposition of $Pt_2(DBA)_3$ (DBA is bis-dibenzylidene acetone) complex. The choice of nanosized "quasi-homogeneous" catalysts for study is because of their high modifier coverage and their unique activity [11–13]. For example, Zuo *et al.* stated [14] that their PVP(poly-N-vinyl-2-pyrrolidone)-cinchonidine modified catalysts "not only afforded superior enantioselectivity (e.g., 98% e.e. for the hydrogenation of methyl pyruvate on a 1.4 nm Pt cluster), but also exhibited novel catalytic properties, e.g., structure insensitivity, which differs completely from their conventional heterogeneous counterparts."

The nature of the increase in EE at initial reaction time (ITP), further decreases and differences in the behavior of conventional Pt/Al_2O_3 and "quasi-homogeneous" cinchonidine stabilized Pt nanoclusters are discussed below. Further, the experimental conditions selected for these experiments were chosen to be mild: room temperature and low hydrogen pressure (2–10 bar) since these are likely to be the most relevant conditions for hydrogenation of α-ketoesters on an industrial scale.

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2. Experimental

2.1. Materials

Pt on alumina (Aldrich 5% Pt, metal dispersion 29%, active metal surface area 3.6 m^2 g^{-1} and concentration of active sites 37 μmol g^{-1} were determined by H_2 chemisorption), cinchonidine (98%, Fluka), acetic acid (99.8% Fluka), ethyl pyruvate (98%, Aldrich), THF (Applichem, 99.8%), formic acid (Aldrich, 99%), acetone and aluminum oxide (4 m^2 g^{-1}, BET) 90 active neutral (0.063–0.2 mm) by Applichem and *n*-pentane (Applichem, min 95%) were used as received. $Pt_2(DBA)_3$ was prepared according to the literature procedure [10] by stirring sodium acetate (Sigma) with DBA (Fluka, ≥96.0%) and K_2PtCl_4 (Acros Organics) in an ethanol (Applichem, 99.9%) water mixture.

In order to purify ethyl pyruvate, 20 mL of it was added to 80 mL of water/*n*-pentane (1/1 by volume) mixture and kept for 2 days in a separation funnel. The *n*-pentane/ethyl pyruvate fraction was separated and *n*-pentane was evaporated in a rotary evaporator. The procedure was repeated two times and the collected purified ethyl pyruvate was found to contain 0.05% R, S ethyl lactate (from the initial 0.5%) by GC.

2.2. Catalyst preparation

2.2.1. Aqueous preparation

A water soluble Pt colloid modified with cinchonidine was prepared according to Bönnemann's literature procedure [10]. Thus, 0.208 g (0.6 mmol) $PtCl_4$ in 160 ml distilled water was reduced with 0.1 M aqueous formic acid (15 ml) under reflux in the presence of dihydrocinchonidine (355 mg or 1.2 mmol). The thus prepared black powder was found to be redispersible in water and acetic acid. This catalyst will be referred to as B – henceforth in this manuscript.

In order to make the catalyst heterogeneous and increase its stability, cinchonidine modified Pt nanoclusters were deposited on non-porous alumina support according to the following procedure.

Three grams of Al_2O_3 was heated at 170 °C under vacuum (10^{-3} mbar) for 16 h and then was cooled to room temperature under vacuum. To this alumina, 16 mg $PtCl_4$ dissolved in 40 mL of acetone solution was added by syringe. After 5–10 min stirring, the initially dark supernatant acetone solution became colorless and an additional 10 mL aliquot of acetone (with 30 mg $PtCl_4$ dissolved) was added by syringe. This procedure was repeated several times, until 200 mg $PtCl_4$ was added, at which point the supernatant no longer changed to colorless. The mixture was then refluxed for 12 h, then the acetone was evaporated and a brown colored powder was collected. $PtCl_4$ adsorbed on Al_2O_3 in this way was reduced in the presence of dihydrocinchonidine by formic acid. Typically, 600 mg Al_2O_3 with adsorbed $PtCl_4$ was stirred in 100 mL of water under a static Ar atmosphere and the solution refluxed. After reflux had begun, 160 mg dihydrocinchonidine in 25 mL 0.1 M formic acid was injected. After 1–2 min the color changed to black, then in 10 min the heat was removed and the mixture was left stirring for 24 h. Afterward, a black powder was separated by filtration and washed with acetic acid, then with water. Finally, the sample was dried in air at 70 °C for 24 h. The catalyst prepared by this method will be referred to as B-S – henceforth in this manuscript.

2.2.2. Organometallic precursor decomposition method

The catalyst was prepared by decomposition of the organometallic complex $Pt_2(DBA)_3$ under hydrogen in the presence of cinchonidine. $Pt_2(DBA)_3$ (402 mg or 0.37 mmol) and an excess of cinchonidine (4.5 g or 15 mmol) were dissolved in 160 mL THF and flushed with Ar for 20 min. The mixture was kept in the glass reactor under 2 bar of H_2 with constant stirring at 300 rpm. After 18 h the black precipitate was collected and washed first with 50 mL pentane, then with a pentane/THF mixture (5:1) until all hydrogenated DBA and excess cinchonidine was removed as monitored by IR spectroscopy. Thus prepared catalysts were found to be redispersible in acetic acid and THF and will be referred as D – henceforth in this manuscript.

2.2.3. Treatment of conventional Pt/Al_2O_3

Commercial Pt/Al_2O_3 sample were heated at 300 °C under vacuum (10^{-3} mbar) for 1 h, then kept for 3 h under flowing hydrogen (100 mL min^{-1}) and cooled to room temperature. Then the required amount was weighed and transferred into a glass reactor with acetic acid and ethyl pyruvate.

2.3. Characterization

Transmission electron microscopy (TEM) micrographs were taken by using a TECNAI F20 instrument. Specimens were prepared by placing a drop of the colloidal (or ethanol with powder of B-S sample) onto a copper grid with a perforated carbon film and then allowing the solvent to evaporate.

IR spectra of powder samples were measured with a Thermo Nicolet Avatar spectrometer in transmission mode, resolution 4 cm^{-1}, number of scans 500. IR pellets were prepared by mixing 100 mg KBr and 1.5 mg sample then pressing into a pellet under a pressure of 10 tons.

Carbon and nitrogen elemental analysis measurements were done on a Carlo Erba NA2500 in the School of GeoSciences at the Grant Institute in the University of Edinburgh. Measurements were repeated several times with an error ~1%. The platinum content was found from TGA after a 30–1200 °C temperature interval under an air flow of 100 mL min^{-1}. An SDTQ600 instrument from TA Instruments was used.

2.4. Hydrogenation of ethyl pyruvate

2.4.1. Reaction

Hydrogenation of ethyl pyruvate was carried out in a 300 mL glass reactor (Parr Instrument GmbH) under a pressure of either 2 or 10 bars of hydrogen at room temperature (22 ± 1 °C). The stirring speed was 300 rpm.

The ethyl pyruvate was added to 70 mL of acetic acid, then the mixture was sonicated for 10 min, Ar was then flushed through the solution for 10 min to remove dissolved air. The required amount of catalyst was added, the mixture was sonicated for 5 min, transferred into the reactor, flushed with Ar for 10 min and finally after the pressure of hydrogen had been stabilized for 10–15 s the initial time ($t=0$) was set and the reaction kinetics were monitored. Around 1 mL aliquots of the reaction mixture were taken at certain time intervals, filtrated with a G4 filter and 1 μL was injected into the gas chromatograph (GC). GC measurements were taken using a Varian 3900 instrument with FID detector and Lipodex-E column.

Cinchonidine modified Pt nanoclusters (B-S) on alumina were used in hydrogenation in the same way as B or D type of catalyst, without thermal treatment.

2.4.2. Determination of cumulative and actual EE

The cumulative enantiomeric excess (EE) was calculated according to the formula $\frac{[R]-[S]}{[S]+[R]}\cdot 100\%$. The actual EE* was calculated by the previously established [7] formula$\mathrm{EE}^{*}_{i+1/2}=\frac{\mathrm{EE}_{i+1}y_{i+1}-\mathrm{EE}_{i}y_{i}}{y_{i+1}-y_{i}}$, where y_i – mol of both ethyl lactates, EE – cumulative (observed) enantiomeric excess.

3. Results and discussion

3.1. Particle size

The TEM pictures (figure 1) of the sample prepared by the DBA (D) method and by Bönnemann's (B) method were magnified and the size of around 100 particles was measured. The number of particles with respect to the particles size for both samples is presented as a histogram in figure 2.

The medium particle size for the (B) sample was found to be 1.2 ± 0.2 nm as compared to the previously reported size of 1.5 nm [10] while for the (D) sample the medium size was found to be 2.4 ± 0.3 nm.

The TEM shows that sample B-S consist of alumina globules fully covered by Pt nanoclusters, the scale of the edge of one globule was increased and presented as an inset in figure 3.

The medium size for Pt deposited on alumina particle the B-S sample was found to be 2.7 nm before exposure to reaction condition (acetic acid, 10 bars H_2, cinchonidine, room temperature) for 16 h and 3.1 nm after (figure 4).

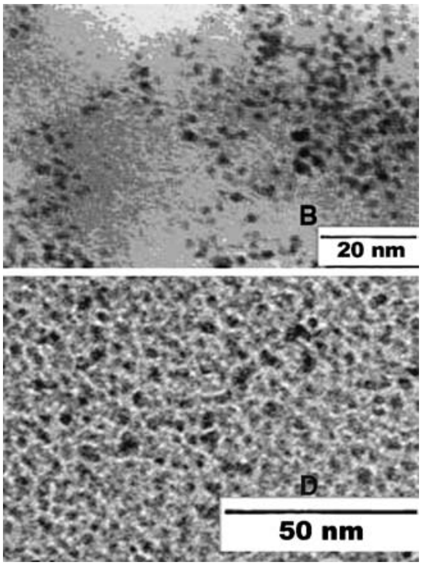

Figure 1. TEM of B- and D-sample.

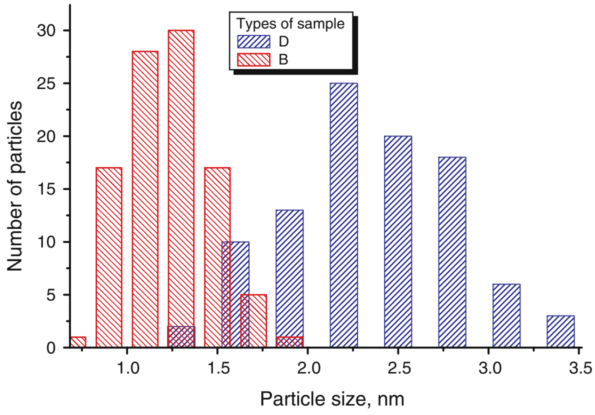

Figure 2. Particles size distribution for B and D samples.

3.2. Elemental analysis

In our studies it was found, that the B-series sample contains 43.5% C, 4.3% N or 50% cinchonidine as an average by carbon and nitrogen. From the TGA, the Pt content was found to be 25% thus differing from the 40% metal content in the original work [11] for 1.5 nm sized Pt cluster, probably because of the presence of moisture/CO/CO_2 and possibly acetic acid (25%).

Elemental analysis of the D-series catalysts before reaction showed 16.6% C and 1.8% N or 20% cinchonidine, by making average between C and N. Sixty-three percent of Pt was found from TGA. The remaining content was attributed to moisture/CO/CO_2.

The content of C and N on the D catalyst after 50 min of reaction was found to be 5.3% and 0.8%, correspondingly or 7% of cinchonidine.

3.3. Hydrogenation experiments

3.3.1. Initial transient period

Under all reaction conditions, summarized in table 2, enantiomeric excess was found to depend on the reaction

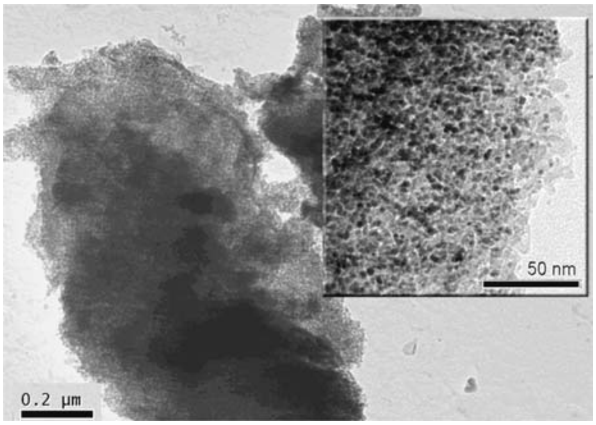

Figure 3. TEM of B-S catalyst after exposure to reaction condition for 16 h.

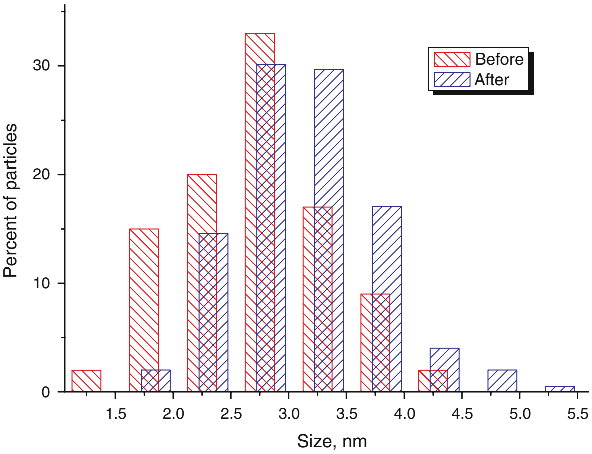

Figure 4. Particles size distribution for B-S catalyst before and after 16 h under reaction conditions (ACOH, 10 bar of hydrogen pressure, no ethyl pyruvate).

time in a manner similar to that shown in figure 5 (other graphs are similar, thus they are not shown, important features are mentioned in the text and in the table 2). During the first moments of hydrogenation (the period of time termed the initial transient period) enantiomeric excess increases to a maximum value (EE_{max}) and then decreases until the entire amount of ethyl pyruvate is converted in the reaction mixture.

Table 1
Composition of B and D catalysts

Sample	% Cinchonidine	% Pt	% Moisture/CO/CO_2
B	50	25	25
D	20	63	17
D after 50 min in the reaction media	7	–	–

Effect of hydrogen pressure
The effect (Exp. 1 and 2) of changing the hydrogen pressure in the reaction system is shown in (figure 5). With an increase of hydrogen pressure from 2 to 10 bar the turnover frequency (TOF) increases by a factor of 10 from 14 to 140 min^{-1}. An increase of TOF could be qualitatively explained as an increase of hydrogen migration from the gas to the liquid phase, but the fact that the maximum enantiomeric excess reached significantly increases from 36% to 78% seems to indicate a specific hydrogen–catalyst interaction, as a consequence of this, the catalyst demonstrates increasing enantioselectivity. A decrease by 4-fold in the time required to reach EE_{max} is observed by changing the pressure from 2 (110 min) to10 (30 min) bar.

Effect of catalyst loading
The decrease of TOF from 99 to 37 min^{-1} with an increase of catalyst loading from 4 mg (13 μmol Pt) to 20 mg (65 μmol Pt) was found in Exp. 3 and 4. Also, the maximum of actual enantiomeric excess (EE^{*}_{max}) has also decreased from 76% to 65%. A possible explanation for this is that the time necessary to reach the maximum enantioselective activation level may not be the same for various catalyst loadings and the full conversion of ethyl pyruvate has already been accomplished. In other words, the number of chiral sites (π-bonded cinchonidine) did not reach the maximum possible value under the 10 bars of hydrogen pressure. It should be noted, that this effect cannot be explained as mass transport phenomena in liquid phase, since according to Minder, Baiker and co-workers [15] the kinetically controlled region lays below 15 g l^{-1} of catalyst concentration while in the Exp. 3 and 4 the maximum catalyst concentration is 0.28 g L^{-1}. In fact, we performed the reactions with 20 mg (Exp. 5A, $EE_{max} = 76\%$, $TOF = 128$ min^{-1}) and 10 mg (Exp. 5B, $EE_{max} = 76\%$, $TOF = 132$ min^{-1}) with conventional Pt/Al_2O_3 and concluded that in our experiments mass transport effect does not limit the reaction. The rate of migration of hydrogen from gas to the liquid phases was the same, since both experiments were performed under the same hydrogen pressure (10 bar).

A similar decrease of EE_{max} with an increase of catalyst loading was found for the B type catalyst (see Exp. 6A and 6B in table 2).

By comparing these results with those reviewed by Studer, Blaser and Exner in 2003 [16] we can see that there are intrinsic differences between the colloids stabilized by chiral ligands and the conventional Pt/Al_2O_3 heterogeneous catalysts which are unmodified prior to introduction to the reaction vessel. In fact, decrease of TOF and maximum enantiomeric excess with an increase of catalyst loading are in contradiction to the results observed for the conventional Pt/Al_2O_3 system, which may be attributed to the fact, that our catalysts have adsorbed cinchonidine already

Table 2
Details of catalysts and reaction parameters

Exp. N.	P_{H2} (bar)	Pt surf. Atoms (μmol)[a]	Type of catalyst and loading (mg)	EE^{*}_{max} (%)	Cinchonidine, concentration (mmol L^{-1})	Time EE^{*}_{max} (min)	slope (min^{-1})	$[EP_0]$ (mol L^{-1})	TOF[b] (min^{-1})
1	2	5.8	D, 4	36	0	110	0.07	2.571	14
2	10	5.8	D, 4	78	0	30	0.07	2.571	140
3[c]	10	5.8	D, 4	76	0	20	0.19	0.514	99
4[c]	10	29	D, 20	65	0	9	0.22	0.514	37
5A[c]	10	1.11	Pt/Al_2O_3, 20	76	1	–	0.24	0.257	128
5B[c]	10	0.56	Pt/Al_2O_3, 10	76	1	–	0.21	0.257	132
6A[c]	10	19.5	B, 20	61	0	3	0.18	0.514	24
6B[c]	10	3.9	B, 4	76	0	–	–	0.514	–
7A[d]	10	2.2	D, 1.5	79	1	30	–	0.514[e]	130
7B	10	2.2	D, 1.5	78	1	30	–	0.514	120
8[c]	10	5.8	D, 4	76	1	55	0.04	0.514	121
9[c]	10	3.9	B, 4	74	1	34	0.07	0.514	42

[a] The number of Pt surface atoms was estimated from the medium particles size according to "full shell" model of Pt nanocluster and from chemisorption on conventional Pt/Al_2O_3.

[b] TOF (min^{-1}) was calculated as normalization a reaction rate (mmol min^{-1}) on number of Pt surface atoms (mmol) in the reaction mixture.

[c] The graph is not shown; important parameters of reaction are presented.

[d] The purified EP was used.

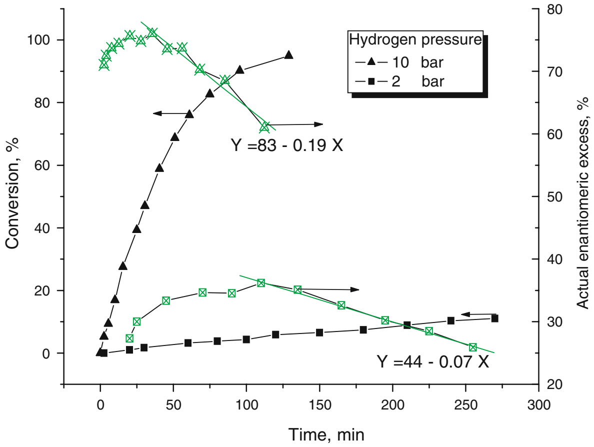

Figure 5. Effect of hydrogen pressure. Experiment 1: 5 mg (13 μmol Pt) D type of catalyst, $[EP_0]$ = 2.571 mol L^{-1}, no free cinchonidine, P_{H2} = 2 bar. Full squares (left axis) – ethyl pyruvate conversion; crossed squares (right axis) – actual EE; line – linear approximation of actual EE decrease. Experiment 2: 4 mg (13 μmol Pt) D type of catalyst, $[EP_0]$ = 2.571 mol L^{-1}, no free cinchonidine, P_{H2} = 10 bar. Full triangles (left axis) – ethyl pyruvate conversion; crossed triangles (right axis) – actual EE; line – linear approximation of actual EE decrease.

on them, whereas the catalyst systems reviewed in the literature are exposed to cinchonidine *in situ* during the reaction.

Role of the ethyl pyruvate in nature of ITP

The ITP was found to be almost independent of the initial concentration of ethyl pyruvate (Exp. 2 and 3). The ITP was found to be 20–30 min in Exp. 2 (20 mL EP) and 20–25 min in the case of Exp. 3 (4 mL EP). EE^{*}_{max} is almost the same value (76–78%) in both experiments, but TOF increased by ≈ 30% with an increase of the initial concentration of ethyl pyruvate.

In order to clarify the role in EE of the initial presence of ethyl lactate (0.5% each S and R isomers) as an impurity in EP, the catalytic hydrogenation reaction with the D type of catalyst was performed with both the unpurified and purified EP. Figure 6 (Exp. 7A, 7B) shows that in this experiment the EE observed is similar for both the purified and unpurified experiments with respect to the reaction time and both demonstrate the same ITP = 30 min and TOF = 120–130 min^{-1}. However, the initial presence of R, S ethyl lactates gives a systematic shift in EE. This shift has a maximum value (≈3%) in initial times (at low conversion) and decreases with time (with increase of conversion). Taking into account the initial concentration of both ethyl lactates, the values of the shift lie within the estimated limit.

In order to show that the presence of EP does not play a significant role in increasing EE, for example as a reagent in side reactions (aldol condensation) reaction [17] we performed a blank experiment in the absence of EP with free cinchonidine under reaction conditions (acetic acid, 10 bar of H_2). However, both B and D samples are unstable with prolonged hydrogen exposure especially at high pressure. Thus, to improve stability, we prepared cinchonidine modified Pt nanoclusters deposited on alumina. The stability of these catalysts was examined by exposing the catalyst to reaction conditions for a time (16 h) exceeding the typical reaction time (~1–2 h). It was observed that after 16 h (figures 3 and 4) the medium particles size increased slightly with a maximum 0.5 nm. This suggests that agglomeration is largely inhibited by immobilizing the nanoclusters.

The B-S catalyst, as prepared, demonstrates (P_{H2} = 10 bar, $[EP_0]$ = 0.514 mol L^{-1}, [cinchonidine] = 1 mmol L^{-1}) EE = 79%, however, after pretreating

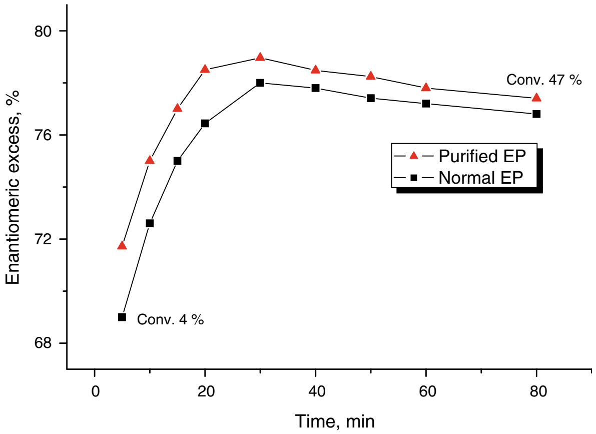

Figure 6. Role of the impurities in the ethyl pyruvate on EE. Experiment 7A: 1.5 mg (4.8 μmol Pt) D type of catalyst, [EP$_0$] = 0.514 mol L^{-1} (purified), [Cinchonidine$_0$] = 1 mmol L^{-1}, P_{H2} = 10 bar. Experiments 7B: 1.5 mg (4.8 μmol Pt) D type of catalyst, [EP$_0$] = 0.514 mol L^{-1}, [Cinchonidine$_0$] = 1 mmol L^{-1}, P_{H2} = 10 bar.

the catalyst for 16 h in acetic acid it demonstrates EE = 84%.

Role of free cinchonidine in ITP

The addition of 20 mg (0.068 mmol) of free cinchonidine into the reaction mixture (Exp. 3 and 8) increases ITP by a factor of almost three (from 20 to 55 min) while $EE^*_{max} \approx 76\%$ remained nearly constant and the TOF increases only slightly. The stability in ee with addition of free cinchonidine was also found for B type of catalyst in out experiments and in original work of Bönnemann [10]. This fact might be explained by competitive formation and disappearance of new chiral sites, as is discussed below.

3.3.2. Post ITP decrease of enantiomeric excess

The decrease of EE during the hydrogenation of ethyl pyruvate has been previously observed both at high (40–100 bar) [18,19] and low (~1 bar) [20] pressures of hydrogen and has been shown to result from the partial hydrogenation of the quinoline (anchor) portion of the cinchonidine. The partially hydrogenated quinoline ring is unable to function as an anchor any longer due to the loss of the π-aromaticity and as a result, the cinchonidine desorbs from the surface resulting in an unmodified catalyst which is not capable of inducing enantioselectivity. Our results support the possibility that this effect also takes place with "quasi-homogeneous" catalysts in the 2–10 bar range.

To the best of our understanding and characterization of the effect, the decay of the actual EE after ITP was linearly approximated and the absolute value of the line's slope was used to determine the stability of catalyst enantioselectivity with respect to the catalyst type and reaction conditions. Thus, in experiments with the same initial concentration of ethyl pyruvate we can easily see in figure 8 where no additional cinchonidine was added (Exp. 3, 4, slope ~ 0.18–0.22 min^{-1}) the rate of decrease of actual enantiomeric excess was observed to be 3–4.5 times greater than with (Exp. 8, 9) free (20 mg or 1 mmol L^{-1}) cinchonidine (slope ~ 0.04–0.07 min^{-1}).

Qualitatively, this effect can be explained by maintaining a more or less constant π-bonded cinchonidine concentration on Pt surface due to the replacement of "old" molecules (with partially hydrogenated quinoline anchor) by "new" molecules of cinchonidine from solution.

3.3.3. Comparison of D, B "quasi-homogeneous" and conventional heterogeneous catalysts

The important principal difference in catalytic behavior of D, B and conventional Pt/Al$_2$O$_3$ catalyst systems is the negligibly small increase of actual (non-cumulative) enantiomeric excess during the reaction in the case of the previously non-modified Pt/Al$_2$O$_3$ (Exp. 5A). This increase of enantiomeric excess was found to be significantly smaller than in the series of experiments with pre-modified catalysts. This indicates the ITP effect is nearly non-existent for the systems which are modified *in situ* under our reaction conditions. That the ITP effect is hardly observed in acetic acid for catalysts without cinchonidine pre-modification is in agreement with the findings of Balazsik and Bartok [7]. In our system, the commercial Pt/Al$_2$O$_3$ shows $EE^*_{max} = 76\%$ which is the same value as was found in Exp. 3 and 8 with the D type of catalysts and also demonstrated similar values of TOF. However, the rate of decrease of the actual enantiomeric excess is 3–6 times higher for the conventional catalyst than for the B and D types of catalyst with the presence of the same amount of free cinchonidine in the reaction mixture (Exp. 8 and 9). Also, the D type of catalyst gave a higher maximum enantiomeric excess and TOF than the B type under the same reaction conditions (compare Exp. 3 with 6B, Exp. 4 with 6A and Exp. 8 with 9) possibly due to the different preparation methods. In fact, the D type catalyst was prepared at room temperature in THF while the B type was prepared at ~95 °C in aqueous solutions. Since it is known that cinchonidine adsorbs predominantly in the flat mode at lower temperatures [21,22], it is possible that this is one of the differences between the B and D type systems.

The two-cycle mechanism proposed by Blaser *et al.* [23,24], based on the assumption that the reaction goes with [R]/[S] = 1 on unmodified sites and with [R]/([R] + [S]) = s on modified sites (near flat adsorbed cinchonidine), explains the observed correlation between EE_{max} and TOF as $EE_{max} = A - B^*TOF^{-1}$, where $A = (2s - 1)k_m/(k_m - k_u)$, $B = A^*k_u$, k_u and k_m are pseudo-first-order rate constants of unmodified and modified cycles. In fact, the graph EE_{max} versus TOF (figure 7) shows a good linear correlation for all our experiments. This means that on modified sites the ratio $[R]/[S] = (1/s) - 1$ is the same for all catalysts and does

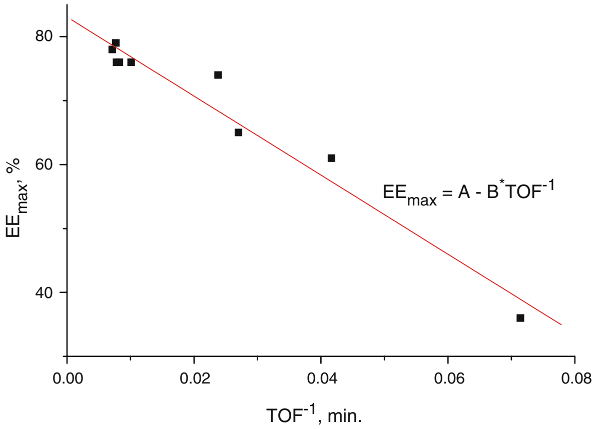

Figure 7. Linear relationship between maximum reached enantiomeric excess and TOF^{-1} for Exp. 1–9.

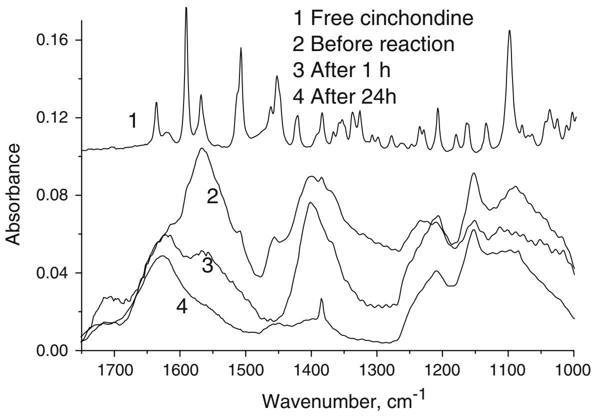

Figure 8. FTIR spectra of the D type of catalyst at different reaction time and spectra of free cinchonidine.

not depend (within the margin of error) on reaction conditions, this seems reasonable because the [R]/[S] ratio is determined by the nature of the interactions between molecules of cinchonidine, ethyl pyruvate and hydrogen on Pt surface. However, the ratio of modified/unmodified sites might strongly depend on experimental conditions, hydrogen pressure (cleanliness of the surface), type of catalyst, concentration of modifier, etc.

3.4. *IR investigation*

The orientation of the cinchonidine species on Pt during the reaction was investigated by measuring the IR spectra of D type catalyst prior to and after 50 min and 24 h under reaction conditions, at 10 bar. After 50 min, the reaction in Exp. 4 ($P_{H2} = 10$ bar, [cinchonidine] = 0 mL L^{-1}, [EP] = 0.514 mmol L^{-1}) was terminated, the hydrogen pressure was released and the reactor opened to ambient conditions. After 1 h the colloidal catalyst precipitated and a black powder was collected, washed three times with acetic acid, dried at 30 °C under vacuum and finally was used for IR investigation. To insure that the washing procedure does not influence results, a control experiment was conducted both before and after washing B and D type catalysts (without exposure to the catalytic reaction conditions). Because the spectra revealed the presence of both the tilted and flat orientations of cinchonidine for all samples it was determined that the washing procedure does not influence the results.

The reaction in Exp. 4 was repeated and when finished, the reaction mixture was kept in the reactor under 10 bar of hydrogen pressure for 24 h after which the colloid solution formed a black precipitate that was collected, washed three times with acetic acid and dried at 30 °C under vacuum and finally was used for IR investigation.

For better visualization, intensity of the spectra (figure 8) of free cinchonidine was normalized. Intensities of the spectra of the D type catalyst are presented as measured. To aid in spectral analysis, the observed vibration frequencies are summarized in table 3.

Analysis of the IR spectra of the D system shows that prior to reaction, cinchonidine is adsorbed in the flat (1) and in two tilted modes: α-H abstracted (2) and in N-lone pair bonded (3). It was found that after 50 min under 10 bar of hydrogen the peaks at 1456 and 1383 cm^{-1} corresponding to the tilted (2 and/or 3) and peaks at 1407 and 1590 cm^{-1} tilted (3) form of cinchonidine are absent and only those IR peaks at 1152, 1209,

Table 3
Vibration band assignment (cm^{-1}) of the cinchonidine spectra of the free cinchonidine, and D type of catalyst before reaction, at 50 min and after 24 h under reaction condition

Free cinchonidine	Before reaction	At 50 min	At 24 h	Assignment[a]
1162	1152	1152	1152	F: 1
1207	1209	1209	1209	T: 2, 3
1383	1383	–	1382	F: 1, T: 2, 3, acetic acid
1420	1402	1402	–	F: 1, acetic acid
1451	1456	–	–	T: 2, 3
1507	1507	–	–	T: 3
1569	1570	1567	–	F: 1, T: 2, 3
1590	1590	–	–	T: 3

[a] F: 1 – flat adsorbed cinchonidine; T: 2 and T: 3 – cinchonidine adsorbed in tilted mode, according to figure 13. Assignment of peaks had been done according to the work of Ferri and Burgi [25], Kraynov [26] and Zaera [27–29].

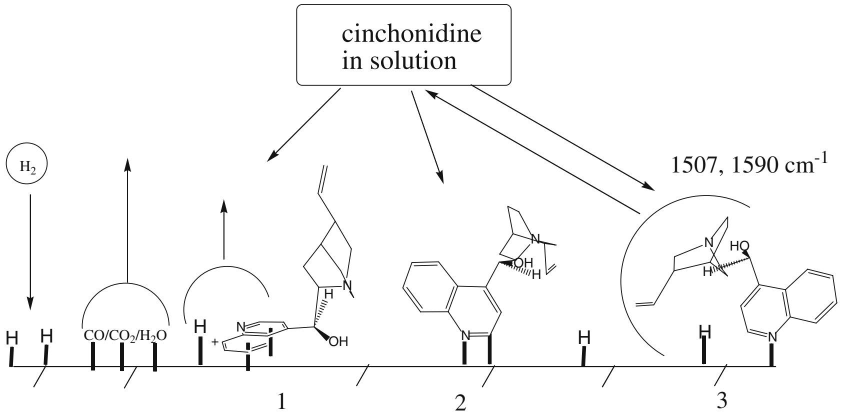

Figure 9. Proposed model of behavior of cinchonidine on Pt under hydrogen exposure. 1 – "π-bonded", 2 – "α-H abstracted", 3 – "N lone pair bonded".

1402 and 1567 cm^{-1} and indicating the flat-mode (1) and tilted mode (2) are observed. After 24 h under 10 bar of hydrogen only peaks at 1152, 1209 and 1382 cm^{-1} remain. The peaks at 1152 and 1209 cm^{-1} could be assigned to flat (1) and tilted (2) modes, whereas the peak at 1382 cm^{-1} corresponds here to the acetic acid.

The absence of the tilted (3) mode of the adsorbed cinchonidine (absence of the peaks at 1590, 1507 and possibly 1456 cm^{-1}) after approximately 1 h of hydrogen exposure indicates that N-lone pair bonded cinchonidine on Pt nanoclusters has a weak adsorption strength with respect to the flat (π-bonded) and α-H abstracted species. This fact has been demonstrated previously in the work of Ferri and Burgi [25] for a thin film of Pt. Further, we have recently demonstrated that the adsorption modes for cinchonidine for both the thin film and nanocluster systems are similar [26].

Collectively, these experimental data of the system have led us to propose the model illustrated in figure 9 for the observed phenomena. During ITP for our Pt nanocluster systems, desoprtion of weakly bound cinchonidine molecules (tilted orientation) is occurring as a result of interaction with hydrogen and possibly solvent, making free space for the formation of new chiral sites via adsorption of cinchonidine in the "flat" conformation thus leading to an increase of EE. When cinchonidine coverage of the Pt surface reaches some minimum (due to hydrogenation and/or desorption) the nanoclusters become unstable and agglomeration takes place as was observed with B and D catalysts.

The addition of free cinchonidine leads to an increase of enantioselective stability of these catalysts and increase of ITP likely due to the replacement "old" to "new" cinchonidine molecules on Pt.

4. Conclusion

For the first time, the ITP was observed and studied for cinchonidine modified Pt "quasi-homogeneous" systems. The ITP was observed at room temperature (22 ± 1 °C), in acetic acid media with catalysts prepared by two different methods (D and B type), with different catalyst loadings (1.5–20 mg), with different ethyl pyruvate concentration (0.257, 0.514 and 2.57 mol L^{-1}) under 2 and 10 bar of hydrogen pressure both with (1 mmol L^{-1}) and without addition of free cinchonidine into the reaction mixture.

The D type of catalyst demonstrated higher EE than B type of catalyst, probably due to the different temperatures used in preparation methods. The ITP was found to be dependent on hydrogen pressure and catalyst loading, increasing from 30 to 100 min with a decrease of hydrogen pressure from 10 to 2 bar. Further, ITP decreases from 30 to 9 min with an increase of catalyst (D type) loading from 4 to 20 mg. ITP was also found to be independent of the initial concentration of ethyl pyruvate in the range of 0.257–2.57 mol L^{-1}. It was also found that cinchonidine modified Pt nanoclusters on alumina (B-S sample) catalyst demonstrates (5–10%) higher EE after treatment under reaction condition without EP.

Addition of free cinchonidine (1 mmol L^{-1}) shows almost no detectable influence on the maximum value of EE and slight increase of TOF, but increases ITP by a factor of three and enantioselective stability of catalyst by nearly 5-fold. The highest EE was also found to be independent on the initial concentration of the ethyl pyruvate and decreases with an increase of the catalyst loading from 78 to 65% in the range of 4–20 mg, probably due to the incomplete chiral activation of the catalyst.

The racemic ethyl lactates as an impurity in EP does not play a significant role in behavior of enantiomeric excess, however they make systematical down shift in EE, which decreases with conversion.

From IR investigation, it was found that after approximately 1 h under 10 bar of hydrogen pressure in acetic acid, the weakly bound species which correspond to cinchonidine adsorption in the tilted ("N lone pair bonded") mode are not observed and only the strongly bound species corresponding to cinchonidine adsorption in the flat and in tilted ("α-H abstracted") mode remain. In other words, "N lone pair bonded" species of the adsorbed cinchonidine are desorbed due to the influence of hydrogen and possibly solvent.

Our results are in line with previously published work of Balazsik and Bartok [7] in which the authors assigned the nature of the ITP to competitive adsorption of reactants, modifier and solvent and supplement it in desorption of weakly bonded cinchonidine adsorbed in tilted "N lone pair bonded" mode. It also has to noted, that the hydrogen effect of cleaning Pt surface from previously adsorbed impurities: $H_2O/CO/CO_2$ and possibly oxygen plays a major role in ITP [4].

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