Review

Heterogeneous asymmetric reactions
Part 40. New data on repeated use of Pt-alumina catalyst during enantioselective hydrogenation of ethyl pyruvate[☆]

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Abstract

The repeated use of Pt-alumina (E4759) catalyst modified by dihydrocinchonidine (DHCD) was studied in the enantioselective hydrogenation of ethyl pyruvate under mild experimental conditions not studied before (hydrogen pressure: 1 bar, temperature: 253–298 K, DHCD concentration: 0.001–0.1 mmol/l) in toluene and AcOH. The effects of different reuse methods, DHCD concentration and temperature on the conversion and enantiomeric excess were studied. In toluene depending on the reaction conditions an "increase in ee on reuse" of 10–20% was observed. This effect was not found in AcOH medium. In our opinion, the phenomenon is an intrinsic feature of the Pt-alumina-cinchona catalyst system, in which the restructuring of the catalyst Pt surface may play an important role.
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1. Introduction

The theoretical and practical significance of the heterogeneous catalytic enantioselective hydrogenation of activated ketones is well-known to professionals involved in the research of heterogeneous catalytic reactions [1]. These results have been reviewed continuously: the first detailed overview was published in 1997 [2] and the most recent one in 2003 [3]. The most extensively studied reaction is the hydrogenation of ethyl pyruvate (EtPy) to ethyl lactate (EtLt) on Pt-alumina catalyst modified by cinchona alkaloids (Scheme 1).

For purposes of practical utilization, knowledge of one of the main advantages of heterogeneous catalytic reactions, namely the repeated use (reuse) of catalysts is also highly important in enantioselective hydrogenations. The results of studies to date, including studies carried out in batch reactors [4–8] as well as continuous measurements performed

in fixed-bed reactors [9–13], have been summarized in the reviews cited above [2,3]. Of activated ketones, studies of this type have been conducted mainly with EtPy as starting material (it has to be noted that some experiments have also been done with ethyl 2-oxo-4-phenylbutyrate and ketopantolactone in continuous mode).

Repeated use of Pt alumina catalysts modified with cinchona alkaloids in EtPy hydrogenation was studied in various solvents (occasionally without solvents) at hydrogen pressures of 5–90 bar. The most important conclusion of these experiments was that the catalyst could be productively reused only if hydrogenation was stopped at ca. 70% conversion, and fresh modifier was also added before reuse, or if the modifier was originally present at high concentrations [6,8].

In order to obtain new information, we initiated experiments to study Pt catalyst reuse in EtPy hydrogenation under mild experimental conditions not studied before (hydrogen pressure 1 bar, room temperature, low modifier concentration). Hydrogenations were carried out in a batch reactor in the two solvents, which are the best for the enantioselective hydrogenation of EtPy, namely toluene and acetic acid.
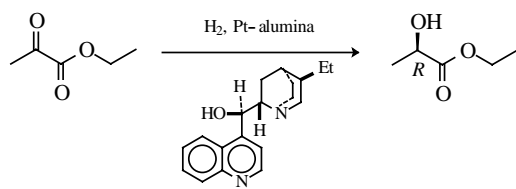
Scheme 1.

Chiral modifiers used were dihydrocinchonidine (DHCD) and cinchonidine (CD).

2. Experimental

2.1. Materials

Cinchonidine (CD), toluene, AcOH and EtPy were purchased from Fluka and from Aldrich. EtPy was distilled before use on a Vigreaux column and was 99 % purity.

The impurities in CD as determined by HPLC are 1.1% quinine and 2.6% quinidine. DHCD was prepared by hydrogenation of CD (Pd/C, 1 N H_2SO_4/H_2O, 1 bar, 298 K) and used after crystallization. A $1\,mmol\,l^{-1}$ DHCD solution was prepared in toluene, and the required volume was added to the reactor. (The $1\,mmol\,l^{-1}$ DHCD solution contained ~1% AcOH, because the solubility of DHCD in toluene is limited.) Because of good solubility of CD in toluene, the solutions containing $1\,mmol\,l^{-1}$ CD can be made up without difficulty.

Based on the data in the literature [2,3], from several catalysts, the one most often used is Engelhard 4759 (E4759). E4759 was pretreated before use in a fixed-bed reactor by flushing with $30\,ml\,min^{-1}$ helium at 300–680 K for 30 min and $30\,ml\,min^{-1}$ hydrogen at 680 K for 100 min. After cooling to room temperature in hydrogen, the catalyst was flushed with helium for 30 min and was stored under air before use.

2.2. Hydrogenation

Hydrogenation was performed in an atmospheric batch glass reactor with volume of 10 ml [14]. The agitator speed was 1200 rpm to avoid the diffusion range. The catalytic system including catalyst and solvent was purged three times with hydrogen and after prehydrogenation (30 min), the calculated amount of modifier and, after 1 min, 0.1 ml of EtPy was introduced and stirred in the presence of hydrogen for the required reaction time. Standard conditions are: 25 mg E4759, 4 or 5 ml of solvent, 1 bar hydrogen, 297–298 K, 1200 rpm, and 0.1 ml of EtPy. The quantification of conversion and ee are based on GC data [14].

Catalyst reuse was performed in the following way: the mixing was stopped, the reaction mixture was left to settle for 30 min, the liquid was removed, and solvent, EtPy and occasionally modifier were added to the reactor. Hydrogenation was repeated as described above.

3. Results and discussion

At the time of discovering the enantioselective hydrogenation of α-ketoesters, Orito et al. [15] recognized the outstanding importance of the state of the platinum catalyst surface in achieving a high ee. For this reason, they pretreated the catalyst at 573–673 K in the presence of hydrogen. In the 25 years that have passed since their discovery, optimization of catalysts and reaction conditions has enabled the achievement of optical purities as high as 97–98% in EtPy hydrogenation [16–18], a result made possible by the resourceful and versatile research carried out at several groups. In order to develop optimal catalyst surfaces, catalyst pretreatment [19–21] and the effects of air and other gases [22–28], ultrasound treatment [17,29], prehydrogenation conditions [22,30], the concentration and impregnation method of modifier [19,29,31,32], particle size and pore size distribution [22,33–37] and support quality [7,14,21,34,35,37–39] have been studied. The results of these far-reaching studies have been reviewed [2,3,40]. The most important conclusions with respect to catalyst reuse are the following: (i) Pt-alumina catalysts with a Pt-dispersion of 0.2–0.3 and a mean Pt particle size of 3–5 nm are the best; (ii) prior to use, the catalyst should be prereduced at 673 K for 1–1.5 h in hydrogen flow; (iii) it is necessary to add fresh modifier for each reuse of the catalyst.

With the information above in mind, we set out to study the behaviour of catalyst E4759 during reuse under mild experimental conditions not tested before. The effects of hydrogenation temperature, modifier concentration, catalyst pretreatment in situ and the choice of the solvent on EtPy conversion and ee were studied.

3.1. Catalyst reuse with different methods in toluene

Hydrogenation rates and ee values observed in reuse procedures carried out in different ways under mild experimental conditions are shown in Tables 1 and 2 and Figs. 1 and 2. The data support the results and conclusions obtained at higher hydrogen pressures [4–8].

Table 1
Repeated use of catalyst for the enantioselective hydrogenation of EtPy

	DHCD (mmol/l)	Time (min)	Rate (mmol min^{-1} g$_{cat}$$^{-1}$)	Conv. (%)	ee (%)
1	0.1	7	6.2	100	85
2	+0	50	0.8	99	23
3	+0	70	0.6	99	10
4	+0	85	0.5	99	0
5	+0	90	0.3	72	0
6	+0.01	35	1.6	98	80
7	+0.01	45	1.1	98	80
8	+0.01	45	1.0	90	80

Standard conditions: 2 ml of toluene.

Table 2

Repeated use of catalyst for the enantioselective hydrogenation of EtPy: effect of the concentration of EtPy on the conversion and on the ee

263 K			298 K			298 K reuse[a]		
Time (min)	Conv. (%)	ee (%)	Time (min)	Conv. (%)	ee (%)	Time (min)	Conv. (%)	ee (%)
45	11	67	5.5	10	61	7.5	14	65
100	22	68	13	21	58	17	25	67
160	32	69	23	32	56	44	46	65
225	43	67	37	43	52	87	66	60
320	55	67	54	54	48	167	89	53
			90	70	42	210	96	50
			142	85	37			

Standard conditions: [CD] = 0.01 mmol/l, 4 ml of toluene, 1 ml of EtPy.

[a] Fresh CD was added.

3.1.1. Hydrogenation of 0.1 ml of EtPy by catalyst reuse

When no fresh modifier is added, both catalyst activity and ee decrease substantially (Table 1), indicating that (i) the quinoline skeleton of the modifier is hydrogenated [8,30,41] and a fraction of the hydrogenated cinchona alkaloid is desorbed, and that (ii) the irreversibly adsorbed cinchona [7,42] does not participate in chiral induction. When fresh modifier is added to the catalyst deactivated in the course of four reuses (Table 1, entries 6–8), the original ee is restored, although reaction rate is significantly reduced due to the deactivation of the catalyst. These two observations (i.e. high ee, decreasing reaction rate) are also confirmed by Figs. 1 and 2. In the experiments shown in Fig. 1, fresh modifier was added before each reuse. The results presented in Fig. 2 verify that high ee can be attained during repeated hydrogenations even without additional modifier, in case if the reaction is stopped at 60–70% conversion.

3.1.2. Hydrogenation of 1 ml of EtPy

The experimental data in Table 2 were obtained under conditions identical with those above, except for the amount of EtPy, which was increased 10-fold. This set of data may be considered as the results of nine reuses; at the same time, it also demonstrates the capacity of the Pt-alumina-DHCD catalytic system (optimization of the experimental conditions for maximal ee was not among the objectives of this experiment). The data in Table 2 allow to conclude that, although hydrogenation is, naturally, quite slow at 263 K, ee remains constant with progressing conversion, indicating that at high EtPy concentrations DHCD is not hydrogenated at this temperature: if it were hydrogenated, ee would decrease due to the low DHCD concentration (0.01 mmol/l) [43]. At room temperature, however, in spite of the considerably higher reaction rate as compared to the case discussed above, ee gradually decreases, which is obviously connected with the gradual decrease in DHCD concentration. The quinoline skeleton of DHCD is probably hydrogenated in spite of the high EtPy concentration. Reusing the same catalyst gives an unexpected and therefore surprising result. After hydrogenation for 142 min, sedimentation, re-
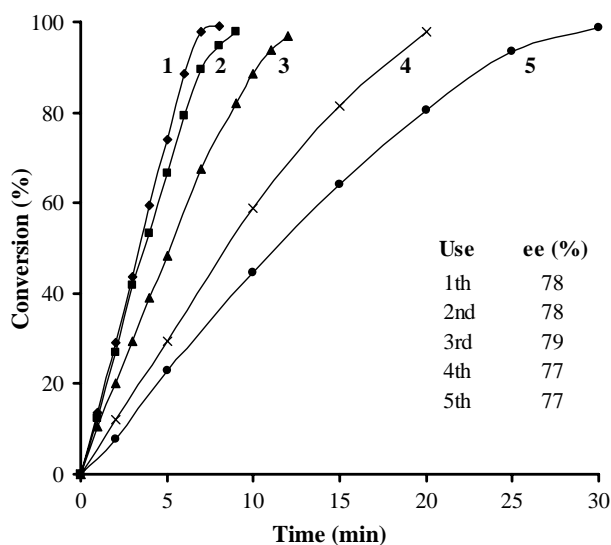

Fig. 1. Repeated use of catalyst for the enantioselective hydrogenation of EtPy (standard conditions, 5 ml of toluene, [DHCD] = 0.1 mmol/l, fresh DHCD was added each time to the reaction solution).
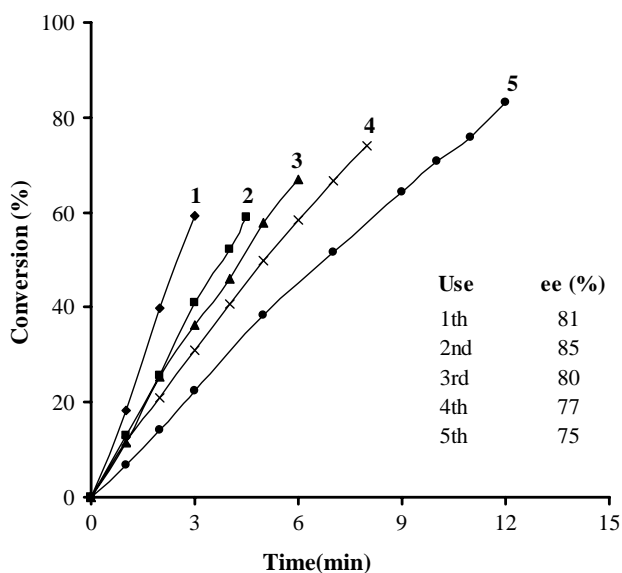
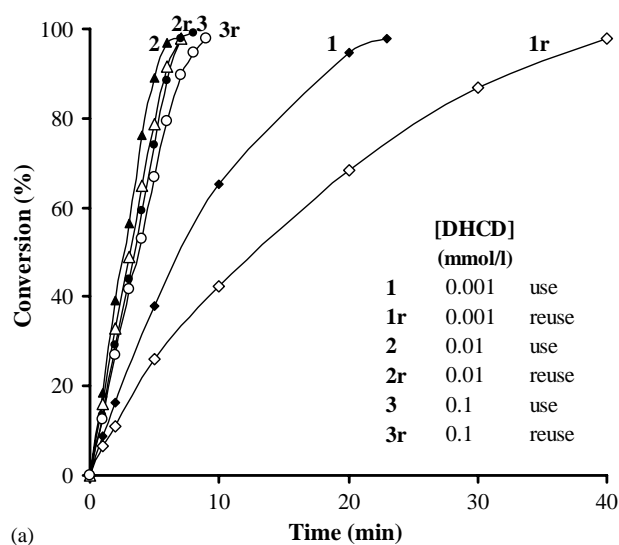| Use	ee (%)
1th	78
2nd	78
3rd	79
4th	77
5th	77

Fig. 2. Repeated use of catalyst for the enantioselective hydrogenation of EtPy (standard conditions, 5 ml of toluene, [DHCD] = 0.01 mmol/l, no DHCD was added for reuse of catalyst).
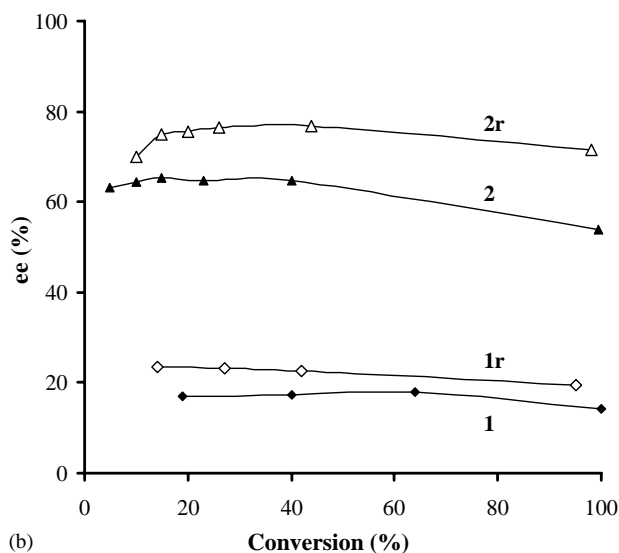
Use	ee (%)
1th	81
2nd	85
3rd	80
4th	77
5th	75

moval of the hydrogenated liquid reaction mixture and addition of fresh reagents (4 ml of toluene, 1 ml of EtPy and 0.01 mmol/l DHCD), hydrogenation was somewhat slower (89% conversion in 167 min for reuse, as compared to 85% conversion in 142 min for first use) but ee increased significantly to 53% as compared to 37% for first use. This novel phenomenon made further studies necessary.

3.2. Catalyst reuse in toluene: effect of DHCD concentration and temperature

Changes in conversion and in ee during the hydrogenation of 0.1 ml of EtPy as a function of temperature (253, 263, and 298 K) and DHCD concentration (0.001–0.1 mmol/l) are shown in Figs. 3–5, comparing the data of the first hy-
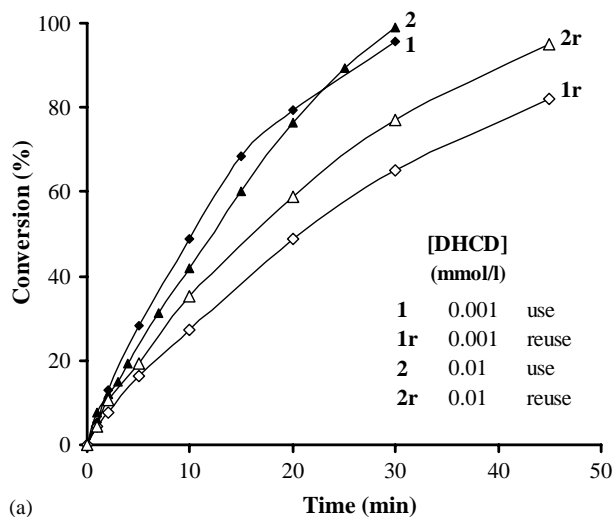
drogenation with those of the reuse. Hydrogenation rate is naturally increased at higher temperatures; modifier concentration, however, has an optimum [43], which itself is temperature-dependent. These data are in agreement with earlier conclusions [2,3]. Hydrogenation is slower during reuse than during the first use of the catalyst, with one exception: at 253 K, hydrogenation with catalyst reuse was faster than the first hydrogenation. The reason for this difference may be that (i) the quinoline skeleton of DHCD was not hydrogenated at this low temperature and, consequently, the catalyst was not deactivated, and (ii) DHCD concentration was higher. As regards ee values, however, according to the data in Figs. 3–5 – just like in the case of measurements using 1 ml of EtPy – the ee values of reuse experiments at 0.001 and 0.01 mmol/l DHCD concentration are significantly higher than those of the first uses, in spite
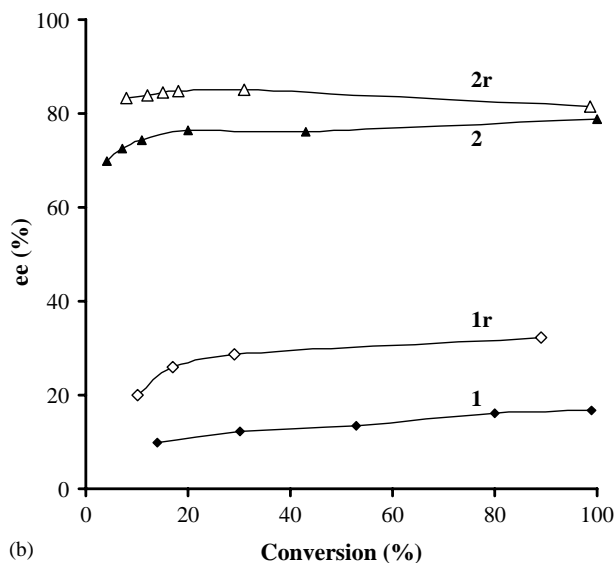
Fig. 3. Repeated use of catalyst for the enantioselective hydrogenation of EtPy: effect of DHCD concentration on the conversion (a) and on the ee vs conversion (b) at room temperature (standard conditions, 5 ml of toluene, fresh DHCD was added for reuse; r, reuse).

Fig. 4. Repeated use of catalyst for the enantioselective hydrogenation of EtPy: effect of DHCD concentration on the conversion (a) and on the ee vs. conversion (b) at 273 K (standard conditions, 5 ml of toluene, fresh DHCD was added for reuse; r, reuse).
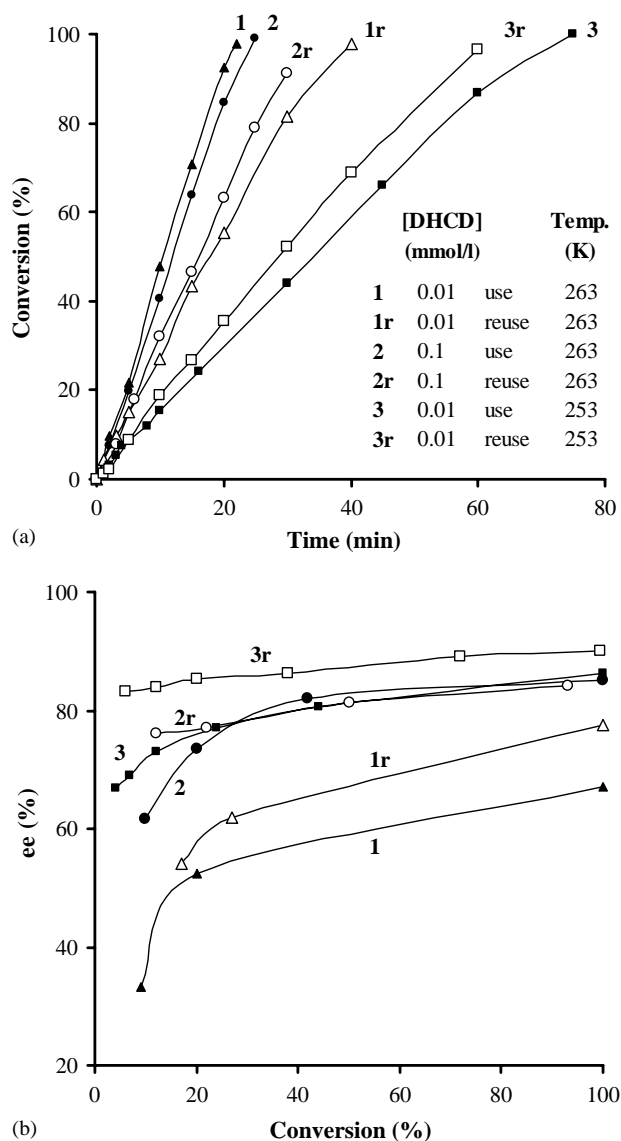
Fig. 5. Repeated use of catalyst for the enantioselective hydrogenation of EtPy: effect of DHCD concentration on the conversion (a) and on the ee vs. conversion (b) at 263 and 253 K (standard conditions, 5 ml of toluene, fresh DHCD was added for reuse; r, reuse).

of EtPy [46,47], at the same time the weak acids produced by various side reactions (e.g. hydrolysis of EtPy) may cause an increase in ee during reuse [7,48].

3.3. Catalyst reuse in AcOH

The data in Table 3 demonstrate changes in conversion and ee in the course of the hydrogenation of 0.1 and 1 ml of EtPy at two different temperatures and DHCD concentrations. Again, the results of first use experiments are compared to reuse. It was already known that EtPy can be hydrogenated to higher ee at lower DHCD concentration in AcOH than in toluene [14,43]. The new observation in the present work is that reuse gave lower ee values in AcOH, i.e. the "increase in ee on reuse" was not observed. This new observation supports the earlier assumption that the mechanism of enantioselective hydrogenation on the Pt-alumina-cinchona catalyst system in AcOH is more different from that in toluene than was originally presumed [43].

4. Interpretation and conclusion of results

In the course of the enantioselective hydrogenation of EtPy on Pt-alumina-cinchona alkaloid catalyst system in toluene under mild experimental conditions, an "increase in ee on reuse" was observed. Namely, repeated hydrogenation following a first hydrogenation (after sedimentation, removal of the liquid reaction mixture and addition of fresh toluene, EtPy and DHCD) resulted in 10–20% higher ee values. In other words, in the course of enantioselective hydrogenation in toluene, ee increases with catalyst use. Theoretically, there is nothing surprising in this observation, since the development of the chiral catalyst surface is based on the interaction of a solid surface and the chiral modifier coming from the liquid phase, and this interaction is slower than a conversion taking place in a homogeneous liquid phase. The experimental data, however, stimulate further thought: for example, the phenomenon is not observed in AcOH. This means that important alterations of probably chemical nature take place on the catalyst surface, which are dependent on numerous factors, such as the competence of the molecules arriving from the liquid phase. Based on the latest experimental results [41,45,49,50], after careful consideration, the following conclusions could be arrived at.

The phenomenon could not be explained by the hydrogenation of DHCD alone. In our opinion, the phenomenon of "increase in ee on reuse" is an intrinsic feature of the catalyst system used, i.e. new chiral centers making higher ee possible are formed. In other words, the catalyst surface is restructured, a process that, after its discovery by Somorjai [51,52], was also justified to be assumed to happen in the Pt-alumina catalyst system modified by cinchonas alkaloids [21,32,44,49] and was recently verified experimentally [45]. It appears obvious today that the surface atoms of the catalyst are continuously reorganized during the reaction as a

of a concomitant decrease in hydrogenation rate. A significant difference of this magnitude was not observed at 0.1 mmol/l DHCD concentration. This so-called "increase in ee on reuse" cannot be explained by hydrogenation of DHCD alone. The phenomenon is probably an intrinsic feature of the Pt-alumina-DHCD catalyst system: new catalytic sites are formed, for the development of which the formerly suggested restructuring of the platinum surface [21,40,44] may be responsible. The role of restructuring is also supported by new experimental data reported most recently by Baiker and co-workers [45].

It must be kept in mind, however, that in non-acidic solvents, side reactions will occur. Namely, the catalyst surface is poisoned due to aldol condensation and oligomerization

Table 3
Repeated use of catalyst for the enantioselective hydrogenation of EtPy in different conditions in AcOH

0.001 mmol/l CD, 298 K, 1 ml of EtPy (1st use)[a,b]			0.01 mmol/l CD, 298 K, 1 ml of EtPy (1st use)			0.01 mmol/l CD, 298 K, 1 ml of EtPy (reuse)			0.001 mmol/l CD, 273 K, 0.1 ml of EtPy (1st use)[c]			0.001 mmol/l CD, 273 K, 0.1 ml of EtPy (reuse)[c]		
Time (min)	Conv. (%)	ee (%)	Time (min)	Conv. (%)	ee (%)	Time (min)	Conv. (%)	ee (%)	Time (min)	Conv. (%)	ee (%)	Time (min)	Conv. (%)	ee (%)
33	9	32	11.5	21	82	10	11	55	1	3	32	1	3.5	23
95	20	24	48	65	79	20.5	26	56	2	4	36	4	9	53
150	32	20	120	91	74	45	47	56	5	8	63	8	13	57
290	45	15	6.5	10	80	75	64	55	10	14	74	16	20	69
360	50	14	13.5	21	81	115	89	52	30	46	82	30	30	70
			22	32	81	150	96	50	60	61	83	60	54	73
			30	47	80							120	83	74
			42	59	80									
			75	77	79									
			150	97	75									

Standard conditions: 4–5 ml of AcOH
[a] Fresh CD was added.
[b] In the reuse of catalyst: time 345 min, Conv. 6%, ee 11%.
[c] 2.5 ml of AcOH + 2.5 ml of toluene in order to keep AcOH dissolved.

result of adsorption/chemisorption steps. In this respect, the presence of trace amounts of oxygen may also play an important role in the reaction studied [21,23,25,28,49,50,53,54]. Chemisorption of trace amounts of oxygen may also play a significant role in our case, i.e. in the course of reuse, the oxygen entering the system via the newly added reaction mixture may oxidize the hydrogen atoms chemisorbed on the Pt surface, thereby generating new Pt clusters, which in turn can form chiral surface sites of higher activity with DHCD via surface interaction, and increase ee. It seems that this effect may not be excluded in the latest studies reported by Baiker and co-workers [45], since during nitrogen pretreatment not only the modifier but also traces of oxygen may affect the restructuring of the Pt surface.

When EtPy was hydrogenated in AcOH, the "increase in ee on reuse" was not observed. This may be due to the operation in this solvent of a different reaction mechanism, in which the alumina compounds formed, described in an earlier publication [14], may also play a role.

For the practical utilization of the repeated use of the Pt-cinchona catalyst system, the reader is referred to the results published by Reschetilowski and co-workers [7] and Vorlop and co-workers [8].

Acknowledgements

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