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The effect of oxygen and the reduction temperature of the Pt/Al_2O_3 catalyst in enantioselective hydrogenation of 1-phenyl-1,2-propanedione

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Abstract

The effect of oxygen and catalyst reduction temperature in enantioselective hydrogenation of 1-phenyl-1,2-propanedione over commercial Pt/Al_2O_3 catalyst was investigated. Dichloromethane was used as solvent. The catalyst was modified in situ with (−)-cinchonidine. Relatively high enantiomeric excesses (65%) of (*R*)-1-hydroxy-1-phenyl-2-propanone were obtained with the solvent used as received, i.e. containing traces of dissolved oxygen and other impurities. Dichloromethane dissociated partially on the Pt/Al_2O_3 surface causing desorption of methane, ethene and HCl from the catalyst during TPD according to mass spectrometric analysis. Under anaerobic conditions the reaction rate was low giving only about 40% enantiomeric excesses of (*R*)-1-hydroxy-1-phenyl-2-propanone. When injecting $5\,mm^3$ of oxygen into the reactor a beneficial effect was observed (i.e. higher reaction rate and enantiomeric excess) in comparison with anaerobic conditions. Poisoning effect of oxygen was observed when injecting $500\,mm^3$ of oxygen into the reactor. Effect of catalyst reduction temperature was studied at three different temperatures (170, 400 and 455°C). Highest reaction rates and enantiomeric excesses were obtained with the catalyst reduced at 400°C. Methane was desorbed from the catalyst at temperatures between 263 and 383°C which could be the explanation for the lower activity of the catalyst reduced at 170°C. It was demonstrated that small amounts of oxygen can have a beneficial effect in enantioselective hydrogenation of 1-phenyl-1,2-propanedione and also that catalyst reduction temperature plays an important role in obtaining high enantiomeric excesses.

Keywords: Enantioselective hydrogenation; Oxygen; Reduction temperature; Platinum

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1. Introduction

The enantioselective hydrogenation of α-ketoesters has been investigated very intensively [1]. There exists quite a few publications in the literature concerning the enantioselective hydrogenation of diones [2–5]. Our model compound is 1-phenyl-1,2-propanedione [6–8], which is hydrogenated to 1-hydroxy-1-phenyl-2-propanone and 2-hydroxy-1-phenyl-1-propanone. Both can exist as (*R*)- or (*S*)-enantiomers. Enan-

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tiomerically pure hydroxyketones are used as intermediates for the synthesis of antifungals and for the synthesis of chiral amino alcohols. The azole antifungals are of high interest as drugs for AIDS related diseases [9] and chiral amino alcohols, e.g. (1*RS*, 2*SR*)-(±)-2-amino-1-phenyl-1-propanol, are used as good vasoconstricting agents and as nasal decongestants [10].

The aim of this work was to investigate the effect of oxygen in enantioselective hydrogenation of 1-phenyl-1,2-propanedione and to find the optimum reduction temperature for the Pt/Al_2O_3 catalyst. Trace quantities of oxygen can inhibit cinchonidine to adsorb too strongly on the catalyst surface [11]. The positive effect of oxygen on enantioselective hydrogenation of diones has been confirmed in 2,3-butanedione hydrogenation [12]. A larger Pt particle size is better for the enantioselective hydrogenation of α-ketoesters, because cinchonidine can adsorb on flat Pt surfaces. In this work we tried to increase the Pt particle size by increasing the reduction temperature of the catalyst.

2. Experimental

2.1. Hydrogenation experiments

The effect of oxygen in enantioselective hydrogenation of 1-phenyl-1,2-propanedione (Aldrich 223034, 99%) was studied by injecting different amounts of oxygen (AGA, 1% O_2, 1% N_2, 98% He or AGA, 99.999% O_2) into the reactor using a 500 mm^3 injection loop. The solvent in these experiments was dichloromethane (Lab-Scan A3508L, 99.8%), the reaction temperature was 25°C and the catalyst was Pt/Al_2O_3 (5 wt.% Pt, Strem, 78–1660). The reactant concentration was 0.01 mol dm^{-3}. The mass-ratio of 1-phenyl-1,2-propanedione to platinum was 25. The catalyst was reduced with hydrogen (AGA, 99.999%) for 2 h at 400°C. All hydrogenation experiments were carried out at 5 bar H_2. The reactant, solvent and (−)-cinchonidine (Aldrich, C8040-7, 96%) were injected into the reactor and the reaction was commenced. In a typical experiment, the mass of the catalyst, reactant and modifier was 59, 74 and 59 mg, respectively. The total liquid volume was 50 cm^3. Stirring rate was 1600 rpm. The following experiments were carried out: (a) dichloromethane was distilled under Ar and the reactant, solvent, and modifier (−)-cinchonidine were mixed under nitrogen. Then the liquid was injected into the reactor, containing the pre-reduced catalyst; (b) same as (a), but 5 mm^3 of oxygen was injected into the reactor at the beginning of the reaction; (c) same as (a), but 500 mm^3 of oxygen was injected into the reactor; (d) same as (a) but the reactant, solvent, and modifier (−)-cinchonidine were mixed under air; and (e) dichloromethane was used as received (without distillation). Samples were analysed by a method described in our previous publication [7].

2.2. Catalyst characterization

The degree of Pt reduction was investigated by X-ray photoelectron spectroscopy (XPS). Before the measurements, the catalyst was reduced at: (1) 455°C for 2 h, (2) 400°C for 2 h or 170°C for 1 h. Then the solvent was injected into the reactor and a catalyst sample was filtered in a nitrogen atmosphere and transferred into the XPS analysis chamber. The XPS analyses were performed with a Perkin Elmer PHI 5400 ESCA system. An unchromatized Mg Röntgen anode (Mg Kα radiation) was used in the spectrum measurements. The equipment energy was 89.45 eV and the analysis steps 0.5 eV.

The Pt particle size was investigated by X-ray diffraction (XRD, a Philips PW1820 diffractometer) and transmission electron microscopy (TEM, using either a Philips CM30T or a Philips CM30UT electron microscope operated at 300 kV). The XRD measuring conditions were as follows: Ni filtered Cu Kα radiation, voltage 50 kV, current 40 mA, automatic divergence slit (irradiated sample length 12.5 mm), receiving slit 0.1 mm, scatter slit 4° with step size 0.020°, counting time 5.0 s per step. The catalyst samples were pre-treated and transferred similarly as in XPS measurements.

Temperature programmed desorption (TPD) of hydrogen was performed in a volumetric flow apparatus with nitrogen–argon (99.5% N_2, 0.5% Ar) as a carrier gas. The catalyst was reduced in three different ways (see above in XPS). The catalyst was then cooled to room temperature and flushed with a carrier gas for 40 min to remove the physisorbed hydrogen. The TPD heating rate was 10°C min^{-1} from room temperature to 650°C. The analyses of the desorbed gases were carried out continuously with a quadrupole mass spectrometer (QTMD, Carlo Erba Instruments). For quantitative measurements, the mass spectrometer was calibrated for the hydrogen signal.

TPD of ammonia was carried out in the same apparatus as TPD of hydrogen. The catalyst was reduced at 400°C with H_2 for 2 h and cooled down to 25°C under hydrogen flow. The catalyst was flushed with He (99.996%) for 45 min and NH_3 (5 vol.% in He) was adsorbed on the catalyst for 45 min. The catalyst was flushed with He for 45 min to remove physisorbed ammonia. The TPD heating rate was 10°C min^{-1} from room temperature to 650°C.

Temperature programmed reduction (TPR) and saturation with dichloromethane was carried out in the same system as mentioned in TPD experiments. The catalyst was reduced with the following temperature programme: 25°C–5°C min^{-1}–400°C (2 h) and during the reduction the formed methane signal at 16 amu/e, was detected by mass spectrometry. After cooling to room temperature the catalyst was flushed for 40 min with the carrier gas (99.5% N_2, 0.5% Ar) and then dichloromethane was adsorbed on the catalyst surface for 30 min. The catalyst was then flushed with carrier gas for 30 min to remove the physisorbed dichloromethane. Then the reduction of the catalyst with hydrogen was started with the following temperature programme: 25°C (50 min)–5°C min^{-1}–400°C and the formed and desorbed HCl, methane, ethane, ethene and dichloromethane were recorded by the mass spectrometer.

The platinum dispersion was measured by using an automatic chemisorption apparatus (Sorptomatic 1900, Carlo Erba Instruments) on catalysts reduced in situ in flowing hydrogen at 400°C for 2 h. The catalyst was purged with nitrogen and evacuated for 1 h at 400°C and the adsorption of H_2 was commenced. Adsorption isotherms were recorded at 25°C and within a pressure range 0.13–13 kPa.

The BET specific surface area was measured with the same apparatus as the chemisorption measurement. The catalysts were degassed for 4 h at 300°C in vacuo prior to the surface area measurement by nitrogen adsorption.

3. Results and discussion

3.1. Qualitative kinetics

The typical hydrogenation kinetics of 1-phenyl-1,2-propanedione in dichloromethane (used as received) in the presence of (−)-cinchonidine is shown in Fig. 1. In the enantioselective hydrogenation of

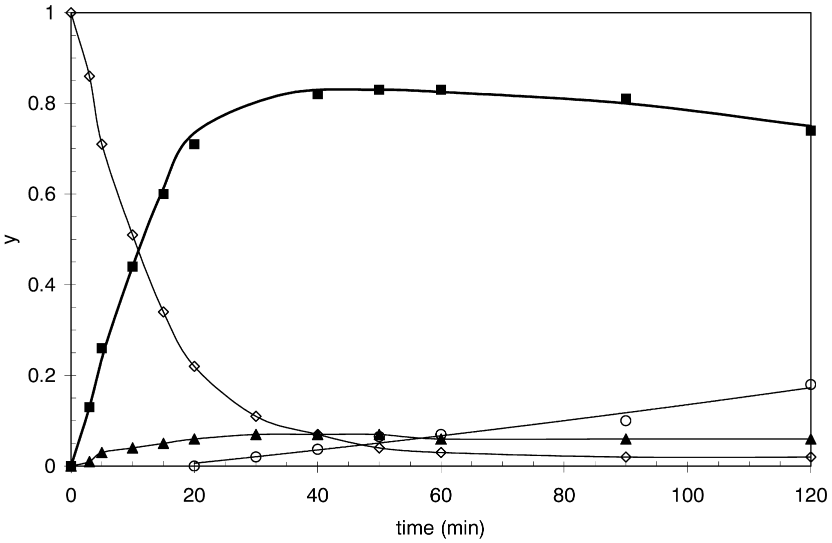

Fig. 1. The hydrogenation kinetics of 1-phenyl-1,2-propanedione in dichloromethane at 25°C and 5 bar H_2: (◇) 1-phenyl-1,2-propanedione, (■) 1-hydroxy-1-phenyl-2-propanone, (▲) 2-hydroxy-1-phenyl-1-propanone, (○) diols.

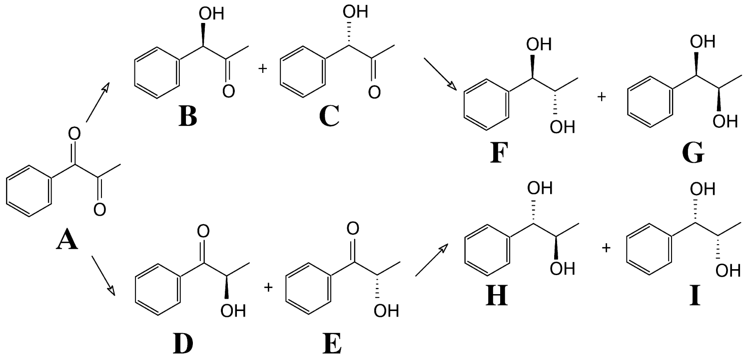

Fig. 2. Reaction scheme.

1-phenyl-1,2-propanedione (**A**) (Fig. 2), the main product is 1-hydroxy-1-phenyl-2-propanone (**B**+**C**), and the regioisomer 2-hydroxy-1-phenyl-1-propanone (**D**+**E**) was formed in minor amounts; the regioselectivity is about 12. This is probably due to the higher steric hindrance of the spherical methyl group compared to the flat phenyl ring. The reaction further proceeded to diols (**F**–**I**). Only minor amounts of diols were formed during 2 h reaction time. The yields of enantiomers (*R*)- and (*S*)-1-hydroxy-1-phenyl-2-propanone and the resulting enantiomeric excess are shown in Fig. 3. The enantiomeric excess (ee) of (*R*)-1-hydroxy-1-phenyl-2-propanone (**B**) was about 65% and it was almost constant with increasing conversion of **A**. These ee's were higher than those obtained by Slipszenko et al. [4] and Studer et al. [5] in the enantioselective hydrogenation of 2,3-butanedione during the first stage of the reaction, when dione was hydrogenated to hydroxyketone, the reported ee's were 42 and 50%, respectively.

Dichloromethane is relatively inert towards platinum surface, it does not chemisorb strongly on Pt(1 1 1) surface according to [13]. The interaction of dichloromethane was investigated by TPR, when

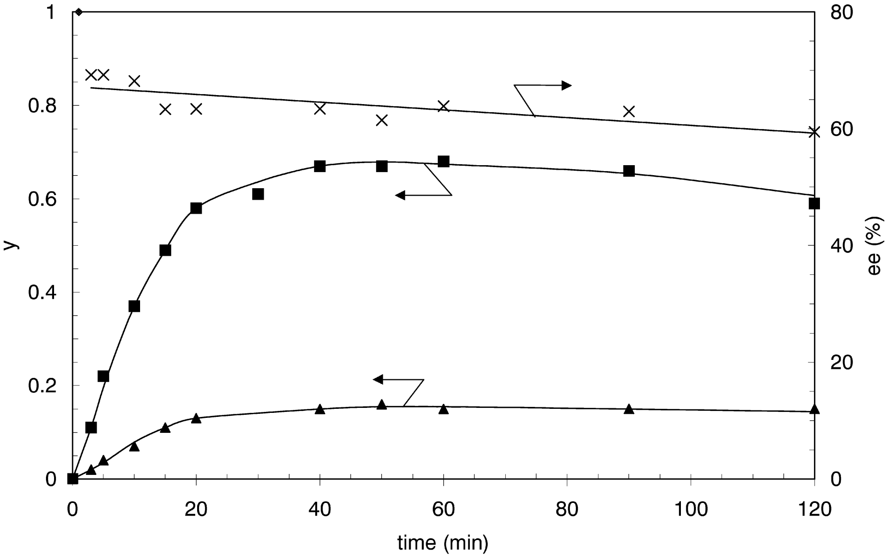

Fig. 3. The yields of (■) (*R*)- and (▲) (*S*)-1-hydroxy-1-phenyl-2-propanone and the (×) ee of (*R*)-1-hydroxy-1-phenyl-2-propanone.

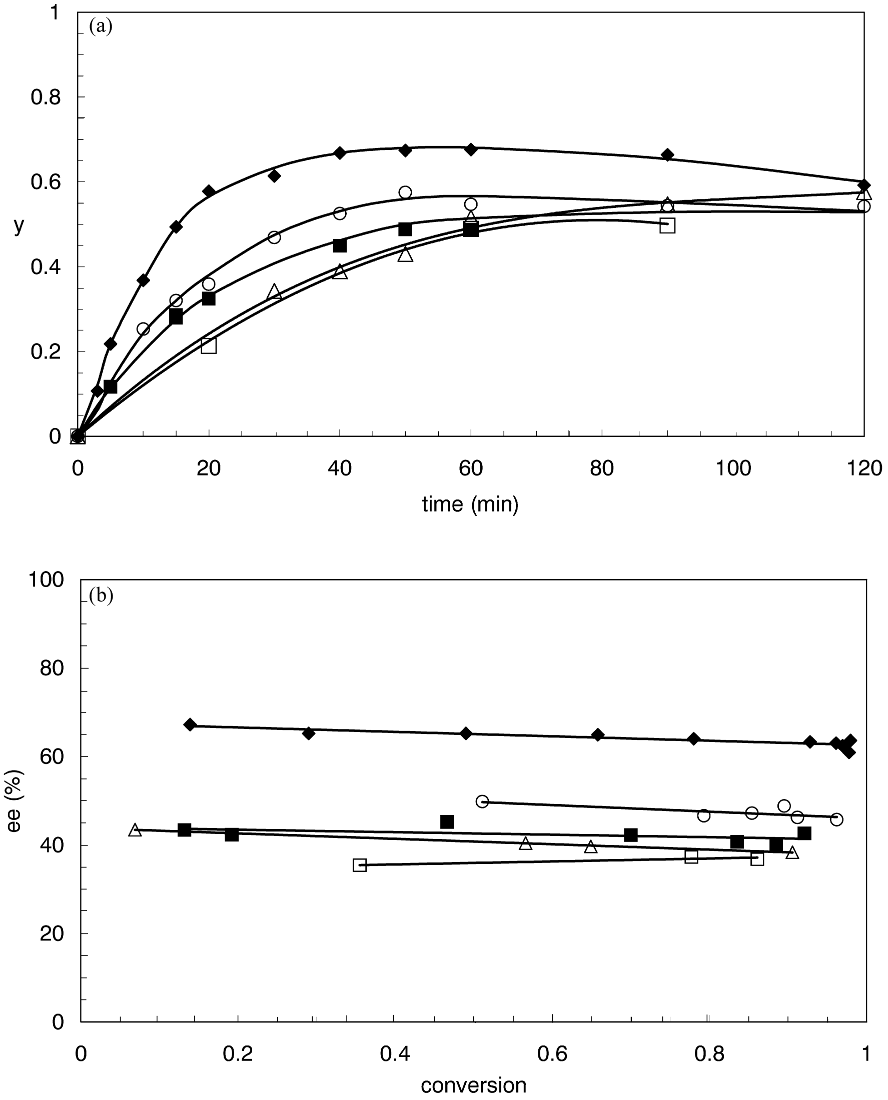

Fig. 4. (a) The yields of (*R*)-1-hydroxy-1-phenyl-2-propanone in the hydrogenation of 1-phenyl-1,2-propanedione. (b) Enantiomeric excess of (*R*)-1-hydroxy-1-phenyl-2-propanone as a function of 1-phenyl-1,2-propanedione conversion. Conditions: 5 bar H_2, solvent dichloromethane, 25°C, modifier (−)-cinchonidine. Symbols: (△) anaerobic, (□) 500 mm^3 oxygen added, (■) 5 mm^3 oxygen added, (◆) solvent used as received, (○) distilled solvent in contact with air.

dichloromethane was pre-adsorbed on the catalyst surface (see Section 2). At the reaction temperature (25°C), dichloromethane dissociated partly and the formation of HCl, methane and ethene was observed. Dichloromethane dissociation occurs by interaction with OH groups on the surface of alumina. This mechanism is similar to the dissociation of dichloromethane on silica [14]. The irreversible dehydroxylation from the catalyst started at 355°C during the TPD and mass spectrometry confirmed the formation of water. The dehydroxylation results in the formation of an incompletely coordinated aluminium atom that can act as an acceptor of electrons, i.e. Lewis acid site. The NH_3-TPD experiments indicated continuous ammonia desorption, and at temperatures between 165 and 650°C strong formation of N_2 and H_2 was observed. The N_2 and H_2 formation is believed to be a result of Pt catalysed dissociation of ammonia and further recombination of N_2 and H_2. The relatively high ee's could partly be due to the acidic milieu where cinchonidine can protonize [15]. The catalyst also had a suitable BET specific surface area and pore diameter for the enantioselective hydrogenation (the BET specific surface area of the catalyst was $95\,\mathrm{m}^2\,\mathrm{g_{cat}}^{-1}$ and the pores were relatively large, 57% of the pore volume located in pores between 10 and 100 nm). The best alumina supports in the enantioselective hydrogenation of α-ketoesters also had large pores [16]. The dispersion of the Pt/Al_2O_3 catalyst was 40.1% according to the chemisorption measurements. The best ee's in the hydrogenation of α-ketoesters have been obtained with supported Pt catalysts with low Pt dispersion (≤20%) [17].

3.2. The effect of oxygen

Contradictory information is presented in the literature about the effect of cinchonidine on reaction rate under anaerobic conditions. The ee's of α-ketoesters have been very low under anaerobic conditions [1] and according to [18], strictly anaerobic conditions result in poisoning of the catalyst by adsorption of the alkaloid on the catalyst surface, resulting in a very slow reaction and low ee. However, according to [1], the presence or absence of cinchonidine had no effect to hydrogenation rate when using anaerobic conditions.

A series of experiments were carried out in order to clarify the effect of oxygen on the hydrogenation rate and the ee of **B**. The yields of **B** are shown in Fig. 4a. When the hydrogenation rate increased, the ee's of **B** also increased (Fig. 4b). The highest ee (65%) was obtained with dichloromethane, which was used as received. When the solvent was used as received, dissolved oxygen was present, which originated from the preparation of the reactant solution under air. We were unable to analyse such a low concentration of dissolved oxygen and no numerical values concerning optimal concentration of dissolved oxygen can be given at present. Trace amounts of other impurities are also present in the solvent used as received, which might have a promoting or inhibiting effect on the ee. Due to the existence of other possible impurities in the solvent, distilled solvent which has been in contact with air was used. The ee of **B** was 50% and the hydrogenation rate was lower than that of the solvent used as received (Table 1). The impurities other than oxygen had a clear beneficial effect on the reaction rate and the ee of **B**. There might be re-oxidation of the Pt surface at room temperature [19] caused in this case by dissolved oxygen, which is normally present in the solvent. When using anaerobic conditions, the ee decreased to ca. 40% and also a lower reaction rate was observed (Table 1). In the literature we have found similar observations; when Pt catalyst is reduced at a higher temperature and there is no exposure of oxygen, the hydrogenation activity is

Table 1
The initial reaction rates and the ee's of (*R*)-1-hydroxy-1-phenyl-2-propanone at 50% conversion of 1-phenyl-2-propanedione with different oxygen additions

Oxygen addition (mm^3)	Initial reaction rate ($\mathrm{mmol\,min^{-1}\,g_{cat}}^{-1}$)	Enantiomeric excess at 50% conversion (%)
[a]	0.40	65
[b]	0.31	50
0	0.14	41
5	0.25	43
500	0.15	36

[a] Solvent used as received.
[b] Distilled dichloromethane in contact with air.

Table 2
The effect of the reduction temperature of the Pt/Al_2O_3 catalyst on the mean platinum particle size determined by XRD and TEM, and the initial reaction rate and the ee of (*R*)-1-hydroxy-1-phenyl-2-propanone

Reduction temperature (°C)	Mean Pt particle size		Initial reaction rate ($\mathrm{mmol\,min^{-1}\,g_{cat}}^{-1}$)	Enantiomeric excess at 50% conversion (%)
	XRD (nm)	TEM (nm)		
170	10.1	–	0.13	24
400	8.3	6.5	0.40	65
455	9	4.7	0.35	44

Table 2
TPD of hydrogen from Pt/Al_2O_3 catalyst. The temperature programme was 25°C–10°C min^{-1}–650°C (20 min)

Reduction temperature (°C)	Peak I		Peak II		Total amount of H_2 (mmol g_{cat}^{-1})
	H_2 (mmol g_{cat}^{-1})	T_m (°C)	H_2 (mmol g_{cat}^{-1})	T_m (°C)	
170	0.008	401	0.009	477	0.017
400	0.011	349	0.018	509	0.029
455	0.016	361	0.013	565	0.029

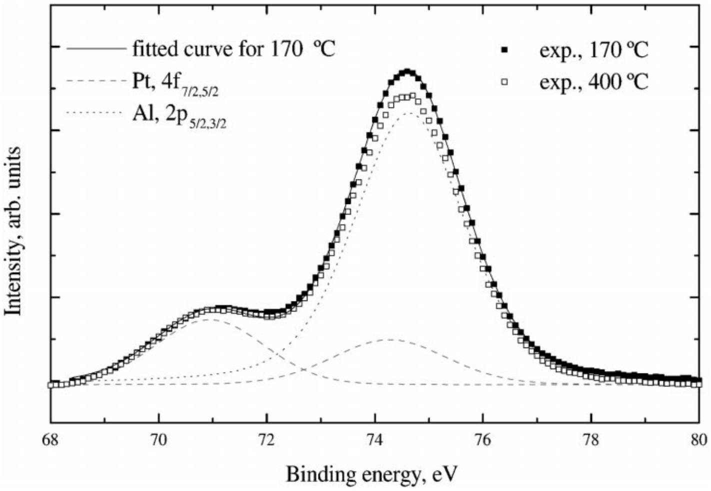

Fig. 5. XPS spectra from the Pt/Al_2O_3 catalyst reduced at 170 and 400°C.

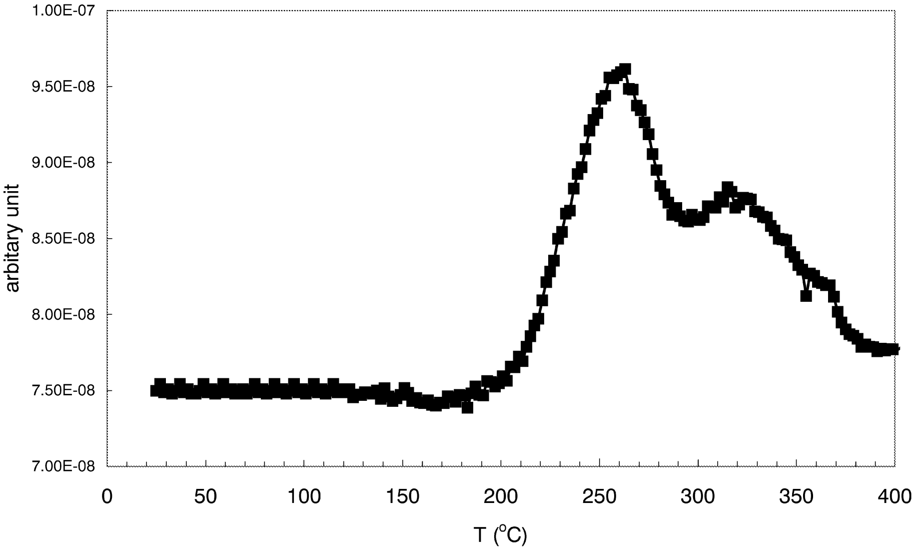

Fig. 6. Methane formation from the catalyst during reduction with hydrogen. The temperature programme was 25°C–5°C min^{-1}–400°C.

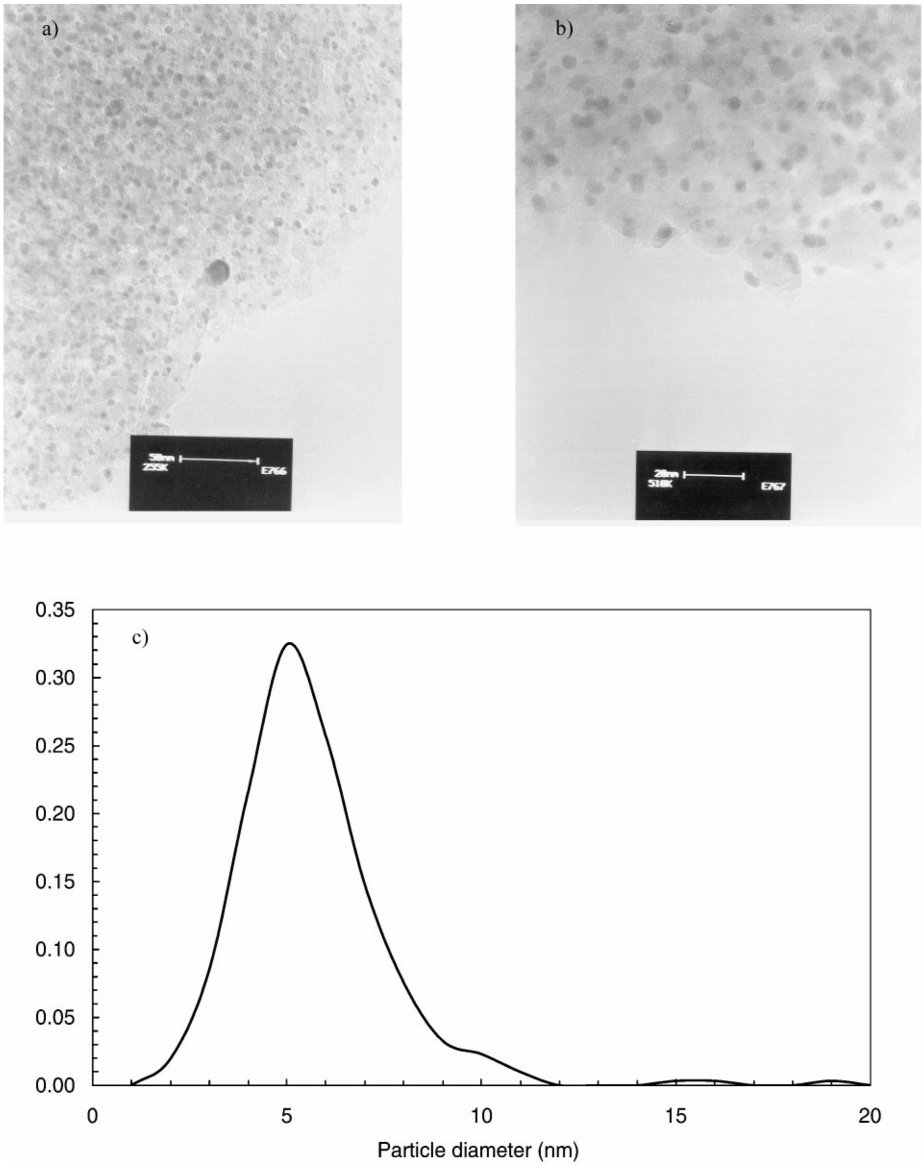

Fig. 7. (a) TEM image of the Pt/Al_2O_3 catalyst reduced at 400°C; (b) high resolution image of the same catalyst; (c) the Pt particle size distribution.

decreased [20]. Slightly higher ee's and reaction rates (43%, 0.25 mmol min^{-1} $g_{cat}{}^{-1}$), in comparison with anaerobic conditions (41%, 0.14 mmol min^{-1} $g_{cat}{}^{-1}$), were obtained when injecting 5 mm^3 oxygen into the anaerobic liquid (Table 1). The second best results were obtained with a solvent distilled under argon and being in contact with air. A poisoning effect of oxygen became apparent, when 500 mm^3 of oxygen was injected resulting in as low as 36% ee. It can be concluded from the above results that there exists an optimum oxygen content giving higher reaction rates and ee of **B** with respect to fully anaerobic conditions.

3.3. The effect of the catalyst reduction temperature

3.3.1. Hydrogen TPD

The amount of hydrogen desorbed from the catalysts reduced at different temperatures could be correlated to the hydrogenation rates (Tables 2 and 3). The total amount of desorbed hydrogen from the catalyst reduced at 170°C was approximately half that obtained from the catalysts reduced at higher temperatures (400 and 455°C). Also, the hydrogen desorption temperature was higher for the catalyst reduced at 170°C than for the other catalysts (Table 3); the reason for this might be due to the desorbed methane. Hydrogen was also more strongly bound to the catalyst reduced at 455°C than the catalyst reduced at 400°C, which explains the higher reaction rate for the latter catalyst.

3.3.2. XPS results

The XPS measurements were carried out in order to characterize the catalysts reduced at 170 and 400°C. In both cases the Pt 3d and Pt 4f peaks clearly indicate that platinum is in metallic state. In the catalyst reduced at 400°C, only a small change in the line shape of the Al 2p and O 1s spectra was observed with respect to the catalyst reduced at 170°C (Fig. 5). No chlorine was found in the Pt/Al_2O_3 catalyst according to XPS measurements.

3.3.3. Organic impurities on the catalyst surface

The reduction of the catalyst with hydrogen (TPR) showed that methane is desorbed from the catalyst between 263 and 383°C, so that the reduction temperature of 400°C is needed in order to get a clean metal surface (Fig. 6). The same trend was observed in XPS results: the mass-ratio C to Pt was 6 in the catalyst reduced at 170°C for 1 h, and 5 in the catalyst reduced at 400°C for 2 h. Organic impurities on the catalyst surface decreased the reaction rate and ee; similar observations are found in the literature [21].

3.3.4. Platinum particle size measurements

According to XRD and TEM measurements the mean platinum particle size was relatively constant when the catalyst was reduced at temperatures of 170–455°C (Table 2). The TEM picture and the Pt particle size distribution from the catalyst reduced at 400°C are shown in Fig. 7. A nearly similar Pt particle size distribution was obtained with the catalyst reduced at 455°C. The main reason for different hydrogenation activities is the difference between hydrogen adsorption states when the catalysts were reduced at different temperatures (see Section 3.3.1) and not the difference in the Pt particle size distributions.

4. Conclusions

Dichloromethane was a suitable solvent for enantioselective hydrogenation of 1-phenyl-1,2-propanedione and it is rather inert towards the Pt surface. However, dichloromethane was not inert towards the Pt/Al_2O_3 catalyst, as methane, ethene and HCl were formed on the catalyst surface. HCl could protonize cinchonidine and thus higher ee's could be obtained. The optimum temperature for catalyst reduction was 400°C; under these conditions the ee of (*R*)-1-hydroxy-1-phenyl-2-propanone was 65%. The lowest reduction temperature (170°C) was not high enough to reduce the organic impurities from the catalyst surface, i.e. methane was desorbed from the catalyst below 383°C. Traces of dissolved oxygen in the solvent were needed for enantio-differentiation.

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