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Enantioselective hydrogenation of ethyl pyruvate Long-term performance of chirally modified Pt/zeolite catalysts

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Abstract

The long-term performance of 5 wt.% Pt/zeolite catalysts (HNaY with different degrees of ion exchange) modified with (−)cinchonidine was studied. The enantioselective hydrogenation of ethyl pyruvate to *R*(+)ethyl lactate was used as the model reaction. The Pt/zeolites are effective catalysts for long-term use, if the chiral modifier is added before each cycle of hydrogenation. The optimal ratio between the amount of catalyst and chiral modifier essentially depends on both the specific Pt surface area of the catalyst and the solvent used. It is found that the use of acetic acid as solvent results in a higher long-term performance than cyclohexane. This is due to the competitive adsorption between the chiral auxiliary and acetic acid on the Pt surface. Furthermore, the acidity of the solvent results in a weakening of the (−)cinchonidine/Pt interaction, which prevents an overloading of the Pt surface area with (−)cinchonidine or its decay products. This effect was determined by means of differential thermal analysis and elemental analysis. When cyclohexane is used as the solvent, the long-term performance is significantly improved by raising the carrier acidity. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Enantioselective; Ethyl pyruvate; Hydrogenation; Pt/zeolite catalysts

1. Introduction

Enantioselective syntheses are most often performed using enzymes [1]. The advantage of such procedures is the very high specificity, which results in the production of almost enantiomerically pure substances. However, the use of enzymatic pathways has some disadvantages, e.g. applications are limited to only a few substrates and in most cases only the naturally occurring enantiomer can be obtained. Other methods have been proposed, as alternatives to the enzymatic pathways, involving homogeneous as well as heterogeneous catalytic processes.

It has been found that homogeneous catalysts are extremely selective and support a wide range of reactions. However, they are very expensive and can be sensitive to the reaction conditions. Furthermore, in most cases the separation of homogeneous catalysts from the reaction products is difficult.

Therefore, chirally modified metal/carrier catalysts have been developed for asymmetric syntheses. These catalysts can be easily separated from the products and it is possible to recycle them. Unfortunately, they do not yield enantiomerically pure products. Another drawback is that these catalysts show no well-defined structure and stoichiometry, which would be disadvantageous for the design of tailor-made heterogeneous asymmetric catalysts.

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In the last few years heterogeneously catalyzed enantioselective hydrogenations have become a topic of considerable interest [2–6]. It has been shown that catalysts based on zeolites are able to act as efficient catalysts for enantioselective hydrogenations [7]. However, the application of these catalysts in industrial processes requires a high long-term stability of the catalytic materials. Therefore, further investigation of the catalytic properties, including optimized reaction conditions, long-term performance, etc. is essential.

In this paper the long-term performance of 5 wt.% Pt/zeolite catalysts (HNaY with different degrees of ion exchange) modified with (−)cinchonidine in the enantioselective hydrogenation of ethyl pyruvate (see Fig. 1) is presented.

In the last few years the research has focused increasingly on the heterogeneously catalyzed enantioselective hydrogenation of α-ketoesters to the corresponding α-hydroxyesters using platinum carrier catalysts and cinchona derivatives as the chiral auxiliaries [8,9].

Only the Pt particles positioned at the *external* surface of the zeolites can participate in the enantioselective hydrogenation, because the cinchonidine used as a chiral modifier is too large to penetrate into the zeolitic pore systems [10]. Additionally the free space around the Pt particles must be large enough for an effective orientation of cinchonidine and ethyl pyruvate. Finally, all Pt particles without ideal size and morphology cause at least partial racemic hydrogenation.

Having chosen appropriate chiral auxiliaries, solvent and reaction parameters from the recent literature [11], the implementation of tailor-made metal/carrier catalysts could be advantageous in order to achieve a good long-term performance by the preservation of enantioselectivity and catalytic activity. In this paper the effects of different parameters such as solvent, acidity of the catalyst support and the ratio of catalyst to (−)cinchonidine on the long-term performance of chirally modified Pt/zeolite catalysts are discussed.

2. Experimental

2.1. Catalyst preparation

The commercial zeolite NaY with a SiO_2/Al_2O_3 molar ratio of ca. 5.2 (Chemiekombinat Bitterfeld) was used as support in the catalyst preparation. H forms were prepared by ion exchange using a 0.1 N aqueous solution of ammonium nitrate (370 K for 2 h) and a subsequent pre-treatment at 723 K for 24 h in an air stream ($10\,l\,h^{-1}$). Three different degrees of ion exchange were achieved (α=0.35, 0.70 and 0.80). The materials were impregnated with platinum using a nitric acid solution of $H_2Pt(OH)_6$. These 5 wt.% Pt/precursors were calcined at a constant temperature (473 or 673 K) for 16 h in a nitrogen stream ($10\,l\,h^{-1}$). The precursors were reduced in a hydrogen stream (3 h at 473 K/673 K, $8\,l\,h^{-1}$) to Pt/zeolite catalysts, denoted as $Pt/H_{0.8}Na_{0.2}Y$, $Pt/H_{0.7}Na_{0.3}Y$, and $Pt/H_{0.35}Na_{0.65}Y$. These reduction conditions proved to be optimal. The stability of the zeolite structure is guaranteed and was verified by XRD [10]. Higher reduction temperatures lead to increasing Pt particle sizes (5–10 nm) and with that to a reduced specific catalytic activity. This is due to the decrease of highly uncoordinated Pt edge atoms between two neighbouring Pt(1 1 1) surfaces. Such active sites can be important for the conversion and catalytic activity but they are less important for the enantioselectivity. The catalysts were used imme-

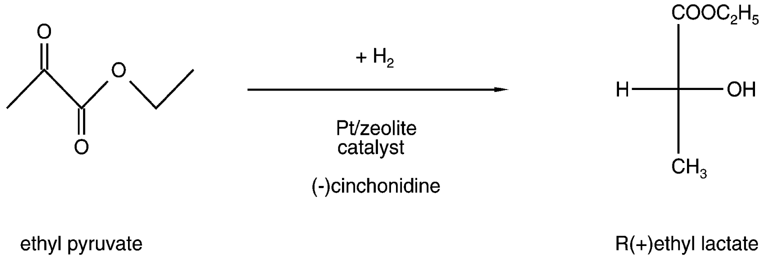


Fig. 1. Model reaction for heterogeneously catalyzed asymmetric hydrogenations.

diately for the enantioselective hydrogenation of ethyl pyruvate.

2.2. Catalyst characterization

The specific surface areas of the Pt/carrier catalysts were determined by volumetric N_2-adsorption at 77 K and the specific Pt surface areas were derived from volumetric CO chemisorption measurements at 298 K as described in [10].

In general it is to be stated that the adsorptive volume (205 $cm^3\,g^{-1}$) of NaY is reduced to 50% after preparation. The following platinum surface areas S_{Pt}, based on the assumption of a monolayer coverage by CO and a stoichiometric proportion of CO to Pt, showed comparable values: Pt/$H_{0.8}Na_{0.2}Y$ (2.4 $m^2\,g^{-1}$), Pt/$H_{0.7}Na_{0.3}Y$ (2.5 $m^2\,g^{-1}$) and Pt/$H_{0.35}Na_{0.65}Y$ (3.0 $m^2\,g^{-1}$). Further characteristic properties of these catalysts in the above-mentioned order are: platinum dispersions: 0.17, 0.19 and 0.22; mean platinum particle sizes: 5.8, 5.6 and 4.7 nm (determined by CO chemisorption); adsorptive volumes: 100 $cm^3\,g^{-1}$ for all three catalysts.

2.3. Catalytic and analytic procedure

The hydrogenations were performed at 293 K and an initial pressure of 7.1 MPa in a 250 ml laboratory autoclave under constant stirring at 20 s^{-1}. Fig. 2 illustrates the flow chart of the equipment used for the catalytic measurements.

In all tests 10 ml ethyl pyruvate was hydrogenated in a mixture with 20 ml solvent (acetic acid or cyclohexane). Four hundred and fifty milligram of the catalyst and 5 mg of the chiral modifier were added. After each reaction cycle the catalyst was filtered off and reused without further treatment. During this procedure a certain amount of catalyst gets lost. In further investigations it was shown that change of the ratio between catalyst and reactant in this range causes no significant change in the activity or selectivity [14]. The conversion of ethyl pyruvate was monitored by measuring the pressure drop over time. The initial reaction rate constant k_0 could also be derived from the pressure drop [12,13].

The final conversion and the enantiomeric excess were determined using gas chromatography. The gas chromatograph was equipped with a 30 m capillary column with permethyl-β-cyclodextrin/polysiloxane as the stationary phase.

The reaction product was finally added to dichloromethane and could be analyzed without any further derivatization.

3. Results and discussion

3.1. Influence of the solvent

An optimized mass-ratio (−)cinchonidine to catalyst was required in order to describe the long-term

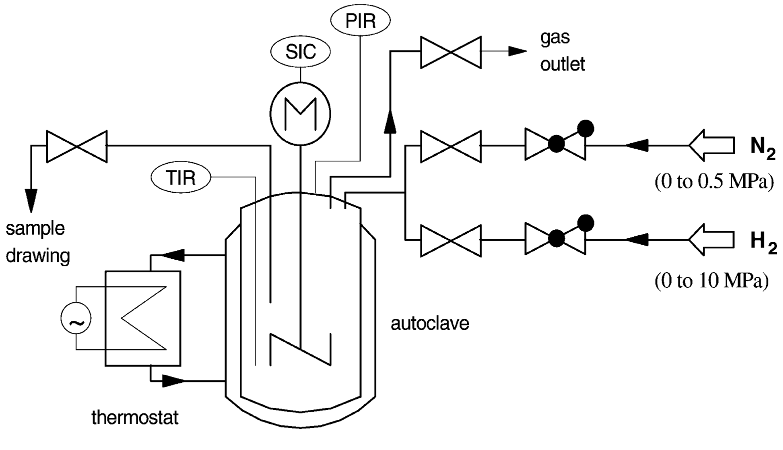
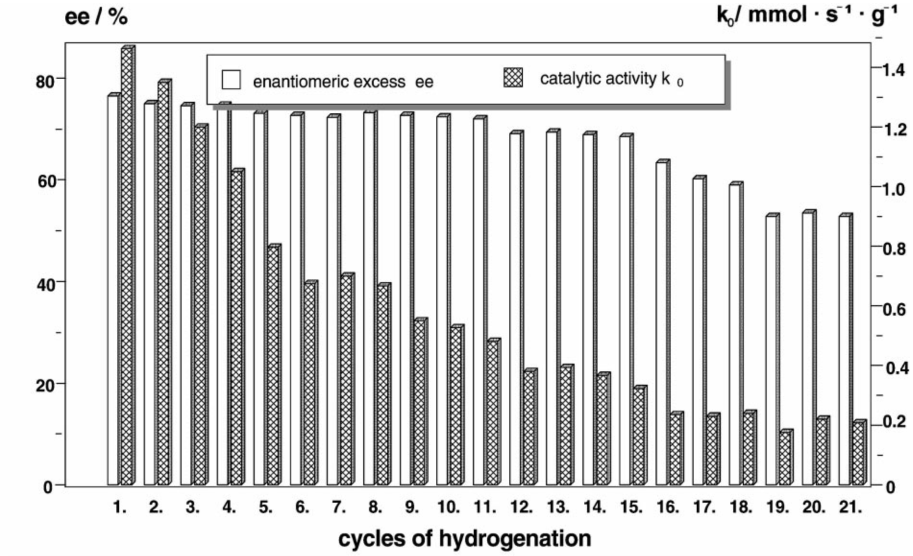


Fig. 2. Flow chart of the equipment used for the catalytic experiments.



catalyst / mg	450	443	434	425	412	404	392	382	374	361	353	342	333	322	313	304	296	291	282	273	260
Modifier / mg	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5

Fig. 3. Long-term performance of $Pt/H_{0.7}Na_{0.3}Y$ (solvent: cyclohexane).

performance of the catalysts. It was found in the first investigation that it is necessary to add a constant amount of the chiral auxiliary (5 mg) after each hydrogenation cycle to obtain a satisfactory selectivity and activity. Furthermore, the filtration of the reaction mixture resulted in the loss of catalyst. Therefore, it is necessary to use a greater amount of the catalytic material when starting a series of measurements.

The performance of the $Pt/H_{0.7}Na_{0.3}Y$ sample with cyclohexane as the solvent led to a nearly constant excess during the period from the first to the 15th cycle of hydrogenation, whereas the catalytic activity decreased (see Fig. 3). It seems that deactivation of the Pt surface takes place after some hydrogenation cycles using cyclohexane as the solvent. This could possibly be caused by an overloading of the Pt surface area with (−)cinchonidine or its decay products.

Fig. 4 illustrates the results obtained by using the same type of catalyst, but acetic acid as the solvent. The chiral auxiliary (also 5 mg) was added in the same manner to each hydrogenation cycle.

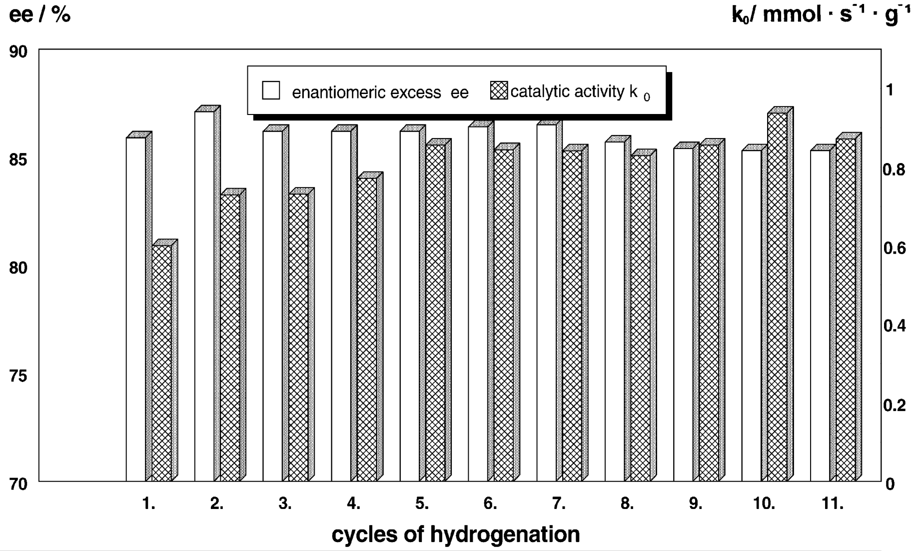
A slight increase in the catalytic activity occurred during the first five hydrogenation cycles. This increase can be explained by an activation of the platinum particles, and takes place over several hydrogenation cycles.

As the catalytic activity and enantiomeric excess were nearly constant, the series of measurements were ended after the 11th hydrogenation cycle.

The catalysts were characterized by differential thermal analysis, before and after a series of measurements to elucidate a possible deactivation of the Pt surface when using cyclohexane as solvent. The relevant thermograms are shown in Fig. 5.

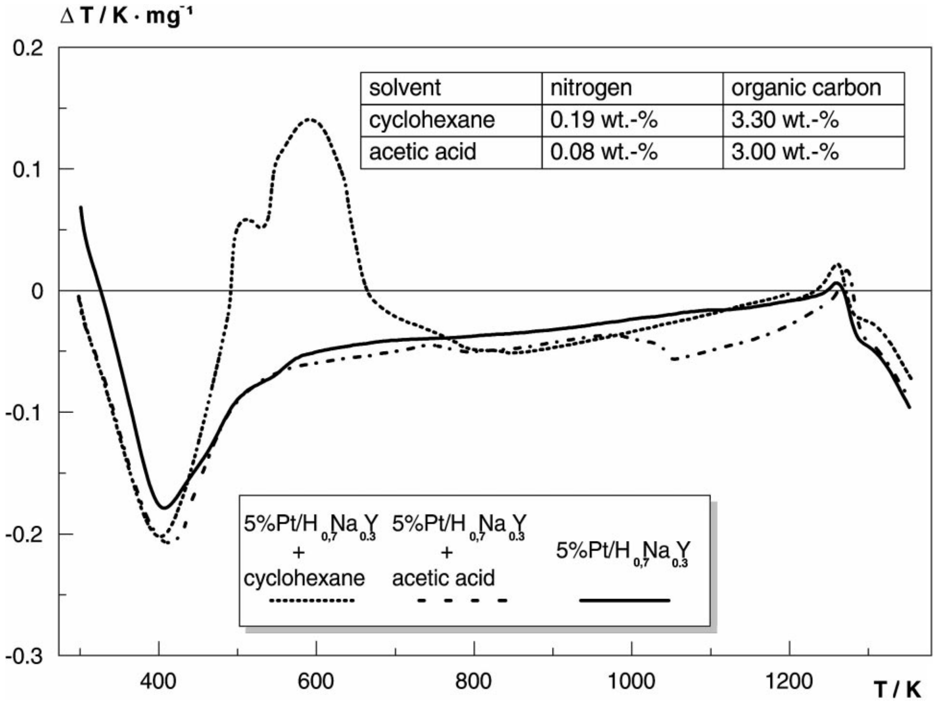
The thermogram of the catalyst used for the asymmetric hydrogenation with acetic acid as the solvent and the thermogram of the fresh catalyst are comparable. But the thermogram of the catalyst used together with cyclohexane as the solvent shows a broad exothermic peak between 450 and 650 K. The conversion of compounds chemisorbed on the catalyst may be the reason for this exothermic peak. Elemental analysis was carried out to obtain more information about the nature of the substances chemisorbed during the hydrogenation (see insert in Fig. 5). A fresh catalyst was used as the reference material.

The amount of nitrogen found on the catalyst used in cyclohexane was twice that on the catalyst used in



catalyst / mg	444	439	435	422	410	402	390	381	378	371	360
Modifier / mg	5	5	5	5	5	5	5	5	5	5	5

Fig. 4. Long-term performance of Pt/$H_{0.7}Na_{0.3}Y$ (solvent: acetic acid).



solvent	nitrogen	organic carbon
cyclohexane	0.19 wt.-%	3.30 wt.-%
acetic acid	0.08 wt.-%	3.00 wt.-%

Fig. 5. DTA thermograms and elementary analysis of fresh and used Pt/$H_{0.7}Na_{0.3}Y$.

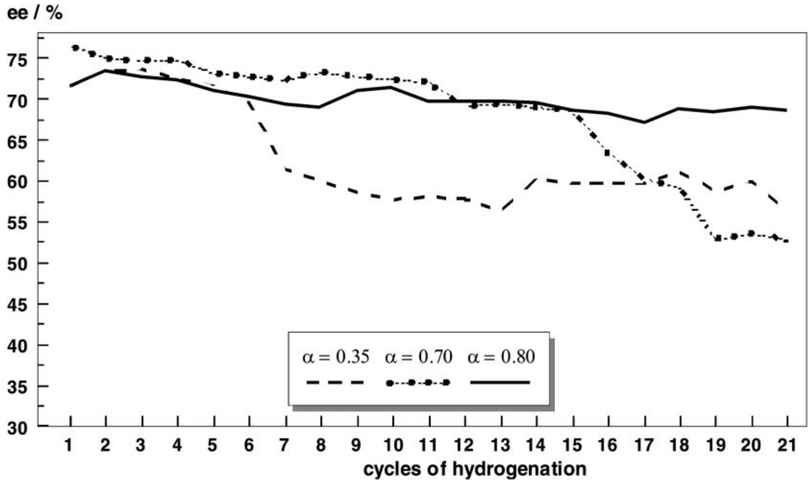


Fig. 6. Comparison of the long-term performance of Pt/$H_{0.35}Na_{0.65}Y$, Pt/$H_{0.7}Na_{0.3}Y$ and Pt/$H_{0.8}Na_{0.2}Y$ (solvent: cyclohexane).

acetic acid, while comparable amounts of carbon were found on both catalysts. As (−)cinchonidine is the only source of nitrogen, the compounds adsorbed on the Pt surface area can be attributed to (−)cinchonidine and its decay products.

3.2. *Influence of the carrier acidity*

To investigate the effects of the acidity of the carrier material, the catalytic measurements were completed by the catalyst samples based on zeolite Y with degrees of ion exchange of α=0.35 and 0.8. By using the method of the Hammett indicators for the indicated exchange degrees the values 1.6, 2.2 and 2.85 meq/g were determined in each case as the total concentration of the acid sites. Cyclohexane was used as solvent and the same reaction conditions were used as previously described.

Although the enantiomeric excesses achieved with the catalyst Pt/$H_{0.8}Na_{0.2}Y$ are nearly constant over all cycles of hydrogenation at a high level, the catalysts Pt/$H_{0.7}Na_{0.3}Y$ and Pt/$H_{0.35}Na_{0.65}Y$ obtained only in the first few cycles a high and constant enantiomeric excesses (see Fig. 6). A significant decrease of the enantiomeric excesses occurred when using these catalyst samples after the 15th and 5th hydrogenation cycles (see Fig. 6). The dependence of the trend in the catalytic activities on the hydrogenation cycles is nearly identical for all three catalysts and it is similar to Fig. 3. But it was observed that the catalytic activity was slightly increased by raising the acidity of the carrier. Therefore, it can be concluded that the deactivation of cinchona-modified hydrogenation sites can be significantly reduced by increasing the carrier acidity.

4. Conclusions

The Pt/zeolites are effective catalysts for long-term use, if the chiral modifier is added before each hydrogenation cycle. Acetic acid as solvent generates a higher long-term performance than cyclohexane. This is attributed to competitive adsorption between the chiral auxiliary and acetic acid. Furthermore, the acidity of the solvent causes a weakening of the (−)cinchonidine/Pt interaction. When using cyclohexane as solvent, the long-term performance is significantly improved by increasing the carrier acidity.

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