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Liquid phase asymmetric hydrogenation on Pt-containing zeolite Y catalysts

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Abstract

5 wt.-% Pt/MNaY catalysts (M = rare earths, Ca, Mg and H with ion exchange degrees of $\alpha \approx 0.65$) combined with (−)cinchonidine as the chiral auxiliary were used successfully for the enantioselective hydrogenation of ethyl pyruvate to R(+)ethyl lactate which resulted in enantiomeric excesses of about 73% (with cyclohexane as the solvent) and 85% (with acetic acid as the solvent). The acidity of the zeolite carrier and the dispersion of the active Pt component do not influence the enantioselectivity of the reaction within the range investigated, but both distinctly control the catalytic activity, which increases with decreasing dispersion and rising acidity. The activities of the catalysts were obtained from kinetic data of the hydrogenation related to the specific surfaces of the active Pt components. The specific Pt surfaces and the dispersion data were derived from volumetric CO chemisorption measurements. 30 to 50 vol.-% of ethyl pyruvate are regarded as the optimal range for the initial concentration concerning both enantioselectivity and reaction rate. Furthermore, initial hydrogen pressure of at least 3 MPa is necessary in order to achieve good enantioselectivities and catalytic activities. The temperature range of 293 to 303 K was found to be optimal. With respect to the dependence of the initial reaction rate on temperature, a change in reaction kinetics was observed between 323 and 333 K.

1. Introduction

During the last few years research has focused increasingly on the heterogeneously catalysed enantioselective hydrogenation of α-ketoesters to the corresponding α-hydroxyesters via Pt/carrier catalysts and cinchona derivates as the chiral auxiliary [1–3].

Besides the variation of substrate, solvent and reaction parameters the significance of the catalytic system with regard to the reaction mechanism represents an area of vital interest. By now it is known that the chiral auxiliary controls the selectivity and also accelerates the reaction. Furthermore, it is assumed that the semi-hydrogenated transition state from the pyruvate to the lactate is stabilized by the cinchona derivate and, thus, being controlled kinetically, the reaction rate is enhanced [3].

The use of an adequate carrier for the catalyst may be a further means of controlling enantioselectivity and catalytic activity. In this context zeolites with their uniform structures manifest exciting properties, for they are already used in petrochemical engineering in order to control catalytic activity and shape selectivity. First results of successful experiments on Pt-containing zeolites as catalysts for the enantioselective hydrogenation of ethyl pyruvate are reported in Refs. [4] and [5].

This paper deals with the effects of Pt dispersion and carrier acidity on both catalytic activity and

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enantioselectivity by using ion-exchanged zeolites Y as carriers for Pt-containing catalysts. Furthermore, the initial concentration of ethyl pyruvate, the initial hydrogen pressure and the reaction temperature are optimized. Kinetic considerations are derived from the dependence of the initial reaction rate on reaction temperature.

2. Experimental

2.1. Catalyst preparation

150 g of NaY (SiO_2/Al_2O_3 ratio≈5.2) were suspended in 600 ml 0.1 normal RE^{3+}, Ca^{2+}, Mg^{2+} and NH_4^+ nitrate solutions and stirred at 343 K for 3 h. RE stands for a technical mixture of neodymium and praseodymium. After purification and drying the zeolites Y were used for further preparation of the catalysts in the following manner.

The zeolites Y were impregnated with 5 wt.-% Pt using an aqueous solution based on H_2PtCl_6 and HNO_3. After having been dried in a drying cabinet (353 K, 24 h), the precursors were tempered in a nitrogen stream (473 K, 10 l h^{-1}, 12 h). During this tempering the NH_4 ion-exchanged zeolite Y was deammoniated to the HNaY. Reduction was carried out in a hydrogen stream (673 K, 6 l h^{-1}, 3 h). The catalysts were used for the enantioselective hydrogenation of ethyl pyruvate to R(+)ethyl lactate immediately after having been reduced.

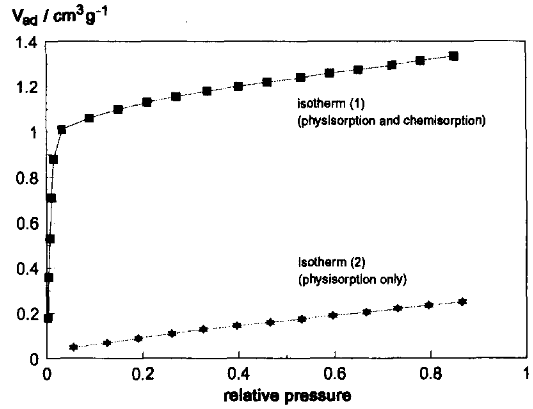

Fig. 1. Determination of the amount of chemisorbed CO by difference measurement (sample: Pt/MgNaY).

2.2. Catalyst characterization

The specific surfaces of the Pt/zeolite Y catalysts were determined by volumetric N_2 adsorption at 77 K (Sorptomatic 1900, Fisons). The results are shown in Table 1.

Furthermore, the specific surfaces of the active Pt components were derived from volumetric CO chemisorption measurements at 298 K (Sorptomatic 1900, Fisons). As CO physisorption is not negligible in this special case, the procedure was divided into two sections: first, measurement of the total CO uptake, corresponding to both chemisorption and physisorption, and then repeated CO physisorption after having been removed from the sample by evacuation at 0.5 Pa and 298 K for 1 h. The amount of chemisorbed CO was derived from the difference between the two CO adsorption uptakes. Two typical isotherms are represented in Fig. 1. Assuming a cross-sectional area for a CO atom of $1.65 \cdot 10^{-19}$ m^2 and a stoichiometric factor

Table 1
Characteristic data of the applied Pt/zeolite Y catalysts

Catalyst	Relative proton activity [6]	Specific surface of the catalyst (m^2 g^{-1})	Specific surface of the active Pt (m^2 g^{-1})	Dispersion
Pt/RENaY	7.0	485	4.1	0.3
Pt/CaNaY	5.2	545	3.0	0.22
Pt/MgNaY	5.6	570	3.8	0.28
Pt/HNaY	10.2	635	2.4	0.17
Pt/NaY	0	500	3.4	0.24

(chemisorbed CO/active Pt) of 1, the specific surface of the active Pt component was calculated from the amount of chemisorbed CO related to the mass of the complete catalyst.

Besides the specific surfaces the dispersions of the active Pt components were calculated assuming a cross-sectional area for a Pt atom of $8.93 \cdot 10^{-20}$ m^2. It was further assumed that the Pt^{4+} cations were completely reduced to Pt^0 in all the previously prepared catalysts. Therefore the specific surface of the active Pt component is directly proportional to the corresponding dispersion. The specific surfaces and the dispersions are listed in Table 1. Table 1 proves that the specific surfaces of the prepared catalysts range in the same order of magnitude. Therefore it is very probable that the various dispersions are caused by the different cations and subsequently different acidities of the ion-exchanged zeolites Y. The relative proton activities given in Table 1 represent a direct acidity scale for the zeolites Y. With regard to the degrees of ion exchange, the values are derived from Ref. [6].

2.3. Catalytic and analytic procedure

Ethyl pyruvate was hydrogenated in a 250 ml laboratory autoclave at a given temperature and initial hydrogen pressure under constant stirring at 1200 min^{-1}. In all tests the liquid/solid ratio was kept constant with 30 ml liquid (different concentrations of ethyl pyruvate in cyclohexane) and 40 mg (−)cinchonidine as the chiral auxiliary being continuously added to 200 mg of the catalyst.

The conversion of ethyl pyruvate was monitored by measuring the pressure drop in relation to time. The amount of ethyl pyruvate converted per time unit was derived from this drop in pressure. It provides the initial reaction rate constant k', if related to the amount of the catalyst and the specific surface of the active Pt component.

Final conversion and enantiomeric excess were determined by using GC MS (Varian GC, ITD-800), equipped with a 30 m capillary column with permethyl-β-cyclodextrin/polysiloxane as the stationary phase (C-Dex-B™, J & W). The reaction product was added to dichloromethane and analysed without derivatization.

3. Results and discussion

3.1. Influence of the initial concentration of ethyl pyruvate

Fig. 2 shows the dependence of the initial reaction rate constant and the enantiomeric excess on the initial concentration of ethyl pyruvate. For this series of measurements 7 MPa were chosen as the initial hydrogen pressure and 293 K as the reaction temperature.

With respect to both catalytic activity and enantioselectivity it is obvious that the best results are obtained in the range of 30 to 50 vol.-% of ethyl pyruvate. This effect can be explained in terms of diffusion and transport of the ethyl pyruvate in the liquid phase. Furthermore competitive adsorption of ethyl pyruvate and (−)cinchonidine on the active Pt plays an important part.

3.2. Influence of the initial hydrogen pressure

The dependence of the initial reaction rate constant and the enantiomeric excess on the initial hydrogen pressure is depicted in Fig. 3. For these

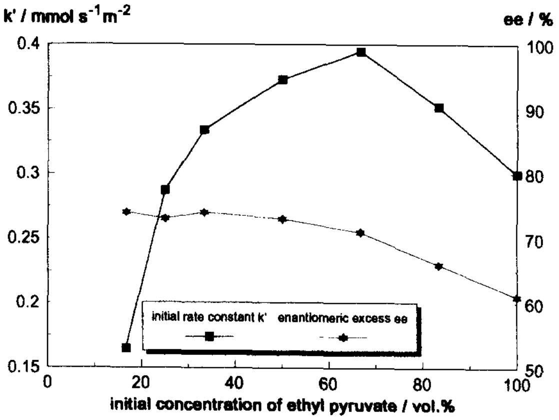

Fig. 2. Dependence of the initial reaction rate constant k' and the enantiomeric excesses on the initial concentration of ethyl pyruvate (catalyst: Pt/MgNaY).

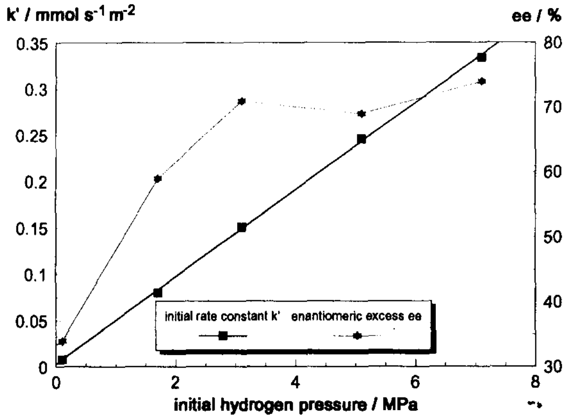

Fig. 3. Dependence of the initial reaction rate constant k' and the enantiomeric excesses on the initial hydrogen pressure (catalyst: Pt/MgNaY).

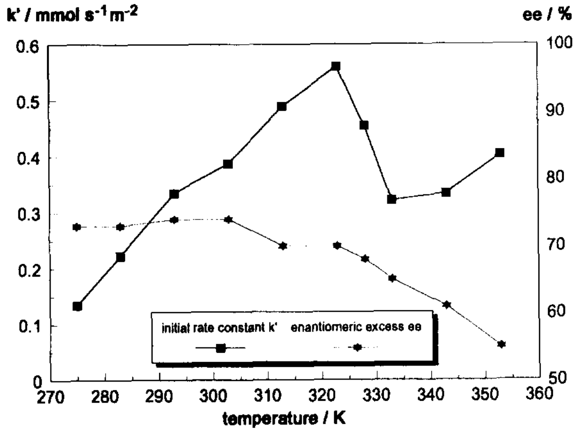

Fig. 4. Dependence of the initial reaction rate constant k' and the enantiomeric excesses on the reaction temperature (catalyst: Pt/MgNaY).

experiments the reaction temperature was kept at 293 K, and 33.3 vol.-% of ethyl pyruvate was used as the initial concentration.

The initial reaction rate constant and, thus, the catalytic activity show a strongly linear increase with the initial hydrogen pressure rising. At least a commencing hydrogen pressure of 3 MPa is necessary in order to achieve high optical yields.

3.3. Influence of the reaction temperature

The series of measurements portrayed in Fig. 4 was based on 33.3 vol.-% of ethyl pyruvate as the initial concentration and 7 MPa as the initial hydrogen pressure. It was found that the increase in catalytic activity with rising temperature is interrupted by a sharp decrease between 323 and 333 K. This effect indicates a change in reaction kinetics. As the enantiomeric excess continuously decreases from this temperature range, it can be concluded that the change in reaction kinetics is due to an impairment of the steric arrangement between the educts and the chiral auxiliary on the catalyst surface.

3.4. Influence of the Pt dispersion and the carrier acidity

The dependence of the initial reaction rate constant and the enantiomeric excess on the specific Pt surface and on the acidity of the carrier is depicted in Figs. 5 and 6. The relative proton activities derived from Ref. [6] are given in parentheses. Differing from the common reaction conditions, acetic acid was used as the solvent in further experiments.

The catalytic activity increases with decreasing specific Pt surface and rising acidity of the carrier, whereas the enantioselectivity is independent of both within the range investigated. Therefore it is useful to select HY zeolites as the carriers for Pt catalysts in order to achieve the highest catalytic activity for the heterogeneous, enantioselective

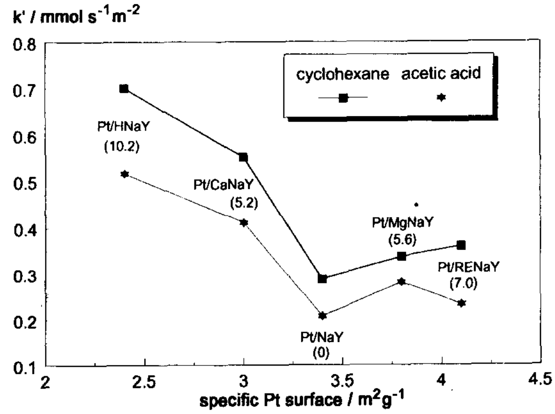

Fig. 5. Dependence of the initial reaction rate constant k' on the specific Pt surface and on the relative proton activity (given in parentheses) of the carrier.

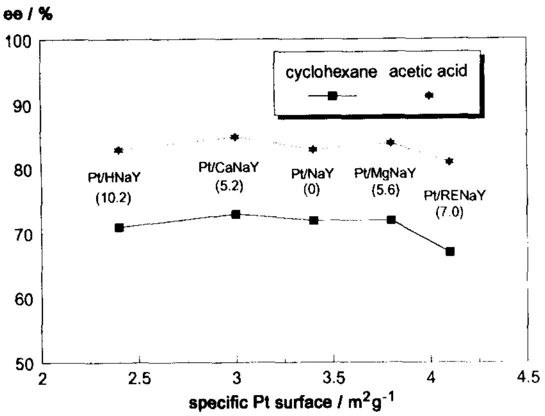

Fig. 6. Dependence of the enantiomeric excesses on the specific Pt surface and on the relative proton activity (given in parentheses) of the carrier.

hydrogenation of ethyl pyruvate. It is also evident that individual control of the catalytic activity is possible over a wide range by varying the solvent in combination with the use of differently ion-exchanged zeolites Y as the carriers. Generally, the significance of the solvent for catalytic activity and enantioselectivity has been treated in Refs. [4] and [5].

Acknowledgements

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