

Research Note

Competition of chiral modifiers on platinum: A transient catalytic and in situ ATR-IR study in continuous reactors

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Abstract

Fundamental aspects of the competition of chiral modifiers on a metal surface were investigated in a continuous-flow fixed-bed reactor using the enantioselective hydrogenation of ethyl pyruvate on $\text{Pt}/\text{Al}_2\text{O}_3$ as an example. The “chiral switch” in the product composition was induced by replacing the modifier (cinchonidine, cinchonine, and quinidine) in the feed. The changes at the catalytic interface were followed by in situ ATR-IR spectroscopy under high-pressure conditions. These studies confirmed the replacement of the chiral modifiers on the metal surface and revealed differences in the adsorption strength and geometry (“flat” and “tilted” species).

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1. Introduction

Heterogeneous catalysts based on the concept of modification of a metal surface by a strongly adsorbing chiral compound are usually less effective than the homogeneous counterparts, but have advantages related to industrial production [1–4]. The easy separation and recycling of the catalyst, and the possibility of continuous operation [5–9], are attractive features for process intensification. In addition, it is possible to change the major enantiomer of the product from (*R*) to (*S*) and back by simply replacing the chiral modifier in the feed. The fundamental aspects of this “chiral switch” are analogous to the nonlinear behavior of modifier mixtures studied in batch reactors by using two modifiers that alone give the opposite enantiomers of the product [10–17]. This nonlinear phenomenon is commonly attributed to the different adsorption strengths of the chiral modifiers on the metal surface. However, the spectacular shifts in ee could not be explained satisfactorily solely by the different surface concentrations of the modifiers [18]. It has been speculated that the dominant adsorption geometries of the modifiers are also different [19].

To understand the competition of chiral modifiers on the metal surface at the molecular level, we analyzed the phenomenon in transient catalytic and in situ spectroscopic experiments in continuous-flow reactors. The hydrogenation of ethyl pyruvate to lactate on a cinchona-modified $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst was chosen as a test reaction [20,21].

2. Experimental

2.1. Catalytic experiments

The experimental setup consisted of three feed lines for the dissolved chiral modifier, the dissolved substrate, and H_2 . The rates of the two liquid flows were regulated by HPLC pumps. The three lines were mixed directly before the reactor. An 8-cm-long Swagelok stainless steel tube with an inner diameter of 1.8 mm (d_i) was used as a continuous-flow reactor. At the front end of the reactor, a quartz wool plug served to disperse the liquid phase and to hold the catalyst bed in place. Before use, the 5 wt% $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst (Engelhard 4759) was reduced at 400 °C in flowing H_2 for 60 min, cooled to room temperature in H_2 in 30 min, and finally flushed with nitrogen. The activated catalyst was immediately transferred to the reactor. Typically, 75 mg of catalyst was used, yielding a bed length (L) of 28 mm. An average catalyst particle diameter of 70 μm (d_p) led to the

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following geometrical ratios of the catalyst bed: $L/d_p = 400$; $d_r/d_p = 25.7$.

The substrate (ethyl pyruvate, Acros, 98%) was carefully distilled under vacuum before use. The chiral modifiers and solvents (Fluka) were used as received. H_2 was delivered by PanGas (99.995 vol%). The reaction conditions were as follows: acetic acid (toluene) solvent, 736 mM ethyl pyruvate, 0.225 mM modifier, 15 bar H_2 , 0.4 ml/min total liquid flow rate, 20 °C. Conversion and ee were determined with a Thermo Finnigan gas chromatograph equipped with a Chirasil-Dex CB (25 m \times 0.25 mm \times 0.25 μ m) capillary column.

2.2. ATR-IR spectroscopy

ATR-IR spectra were collected using a Bruker Optics IFS-66/S spectrometer equipped with a liquid nitrogen-cooled MCT detector and a commercial ATR accessory (Optispec, Switzerland). Toluene (Fluka, 99.7 vol%) was dried over molecular sieves; N_2 was provided by PanGas (99.999 vol%). The Pt/Al_2O_3 catalyst was suspended in 1.5 ml of water, placed on a ZnSe internal reflection element (IRE; 52 \times 20 \times 2 mm, Crys-tran Ltd, England) and dried overnight. The catalyst powder film was reduced at 350 °C before the measurement with the activation procedure described previously. The Pt/Al_2O_3 thin film was prepared on a Ge IRE (52 \times 20 \times 2 mm; Komlas, Germany) by electron beam vapor deposition as described elsewhere [22]. The IRE was fixed in a stainless flow-through high-pressure ATR-IR cell, designed and manufactured in-house. The temperature in the cell was regulated by a thermostat. After mounting the cell, the sample compartment was purged with nitrogen for 3–4 h. Then, N_2 -saturated toluene was flown over the coated IRE for 60 min, followed by H_2 -saturated solvent to clean the surface for 10 min. The chiral modifier dissolved in toluene was then added for the next 30 min before being replaced by the second chiral modifier for another 30 min. All experiments were carried out at 10 bar. The total liquid flow (0.4 ml/min) was regulated using a HPLC pump, and the same concentrations of modifier and substrate were used as in the catalytic experiments. Spectra were acquired by co-adding 300 scans at a resolution of 4 cm^{-1} . Water vapor and CO_2 signals were subtracted when required.

3. Results and discussion

Three different cinchona alkaloids were applied as chiral modifiers in trace amounts, at a modifier-to-pyruvate molar ratio of 307 ppm. Platinum modified by quinidine (QD) and cinchonine (CN) gave the (*S*)-lactate in excess, and that modified by cinchonidine (CD) gave the (*R*)-lactate in excess. When QD was used, the ee in the effluent of the continuous-flow fixed-bed reactor stabilized at around 66% (Fig. 1). After QD was replaced by CD in the feed, the (*R*)-enantiomer formed in excess within 5 min and the ee increased gradually to 89%. (Note that under optimized conditions, both CD and QD afford up to 97–98% ee in batch reactors [18,23] and around 90% in continuous-flow reactors [5].) In the reverse case, CD was fed

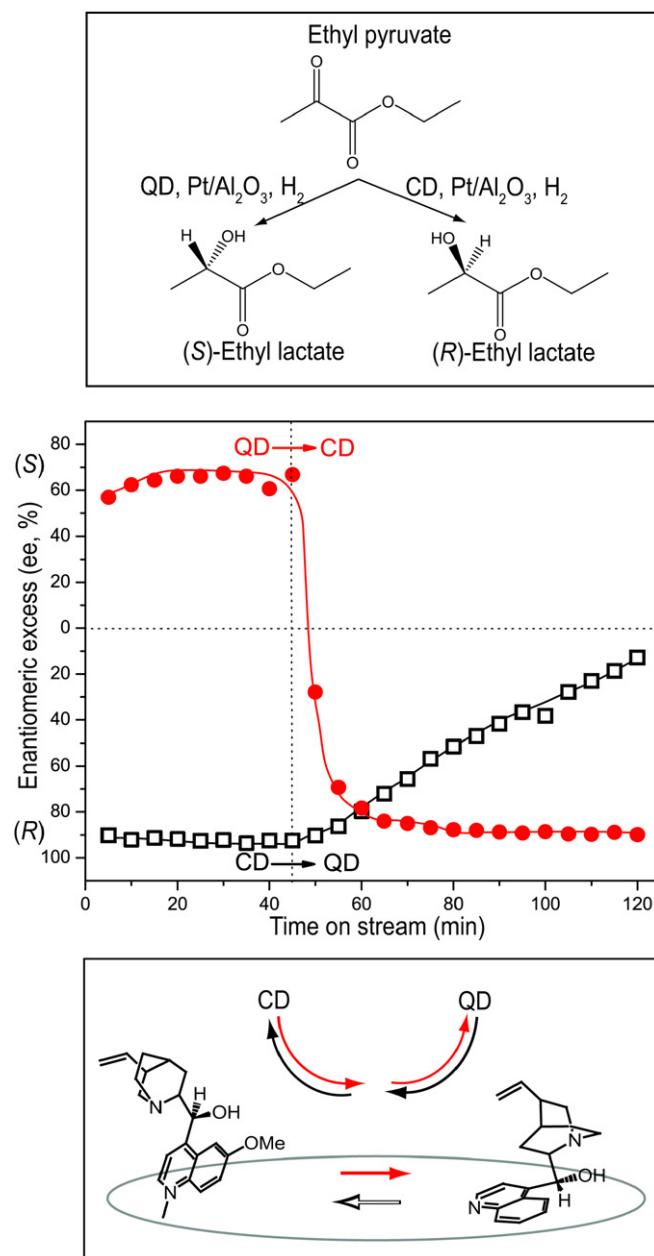


Fig. 1. Top: Major enantiomers in the hydrogenation of ethyl pyruvate on Pt/Al_2O_3 modified by cinchonidine (CD) or quinidine (QD). Middle: Switch of the major enantiomer by replacement of QD with CD (●) or CD with QD (□) in the continuous hydrogenation of ethyl pyruvate in acetic acid. The vertical dashed line indicates the time when the second modifier reached the catalytic bed. Bottom: Different adsorption geometries of the competing modifiers on the Pt surface.

first (Fig. 1), and after switching to QD, the shift in ee was slow and incomplete even after 75 min.

In an analogous experiment, replacement of CN by the pseudoenantiomer CD resulted in a rapid chiral switch from 86% (*S*)-lactate to 82% (*R*)-lactate. Replacement of CD by CN was slower, but still faster than the switch from CD to QD (Fig. 1). It is very likely that the variations in the dynamics of the chiral switch can be traced to differences in the adsorption strength of the modifiers at the metal surface. Based on these experiments, a relative order of adsorption strength of $CD > CN > QD$ may

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