

Alumina-catalysed degradation of ethyl pyruvate during enantioselective hydrogenation over Pt/alumina and its inhibition by acetic acid

D. Ferri, S. Diezi, M. Maciejewski, A. Baiker*

*Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology,
ETH Hönggerberg HCI, Wolfgang Pauli Strasse 10, CH-8093 Zurich, Switzerland*

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Abstract

In situ ATR-IR spectroscopy combined with catalytic hydrogenation, ex situ DRIFT spectroscopy and pulse thermal analysis have been applied to investigate the fate of ethyl pyruvate during enantioselective hydrogenation on Pt/Al₂O₃. ATR-IR investigations indicate that besides platinum-catalysed decomposition/polymerisation ethyl pyruvate can also undergo alumina-catalysed degradation reactions such as aldol type condensation leading to polymeric surface species. Related DRIFT and thermoanalytical measurements of the catalyst after use in enantioselective hydrogenation at different conditions corroborated that side reactions occur irrespective of pressure, solvent and presence or absence of chiral modifier (cinchonidine). The presence of (C=O)- and (C=C)-containing species and of carboxylates were observed during ATR-IR measurements and on catalysts recovered after use in hydrogenation. The carbon content of these species amounted to ca. 3 wt.% of the used catalyst, as determined from the CO₂ evolution upon combustion. Interestingly, acetic acid, the most suitable solvent for the enantioselective hydrogenation of ethyl pyruvate, was found to suppress the degradation reactions, adding a new facet to the beneficial role of this solvent. The implications of the occurrence of degradation reactions of ethyl pyruvate on Pt/Al₂O₃ on the behaviour of this catalytic system in enantioselective hydrogenation are discussed.

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1. Introduction

Beside the possible industrial relevance for the production of key chiral intermediates, the enantioselective hydrogenation of activated ketones over cinchona modified Pt/Al₂O₃ [1] offers the technologically fascinating opportunity to generate enantioselectivity by adsorbing a chiral compound, termed modifier, onto the metal surface [2]. A remarkable feature of this catalytic system is the rapid increase of enantiomeric excess (e.e.) in the early stage of reaction, i.e. the initial transient period, which is often accompanied by an enhancement of the reaction rate [3,4]. During this period the hydrogenation reaction is found to be typically accelerated up to 100-fold with respect to the unmodified reaction [5]. Although the rate acceleration is believed to be a general

feature of the asymmetric hydrogenation mediated by a chiral modifier on a metal surface, some exceptions exist for Pt [6–8] and particularly for other noble metals, such as Pd [9] and Rh [10]. The fact that the reaction is highly sensitive even to minute changes in the experimental conditions and the difficulty to accurately follow the reaction during the initial transient period with conventional analytical methods have generated considerable debate about the nature of the rate acceleration [11–15].

Ethyl and methyl pyruvate and to a lesser extent α,α -trifluoroacetophenone undergo degradation reactions when in contact with the metal and the support. The two alkyl pyruvates decompose to CO and short hydrocarbon fragments on Pt [11,16] (and on Ni [17]), or polymerise in vacuum following aldol reaction on Pt in the absence of hydrogen [18] and in solution in the presence of the chiral modifier cinchonidine [19], or hydrolyze [20]. Several adducts originating from the base-catalysed ethyl pyruvate condensation were identified in the reaction mixture using ESI-MS [21]. Most recently, studies

* Corresponding author. Tel.: +411 6323153; fax: +411 6321163.

E-mail address: baiker@chem.ethz.ch (A. Baiker).

based on cyclic voltammetry and selective site poisoning performed on Pt/graphite revealed that polymerisation of ethyl pyruvate occurs preferentially at step sites and that the alkaloid inhibits propagation of polymerisation on platinum [22].

Some components of the reaction system are known to act in a beneficial way by suppressing undesired side reactions. For example, cinchonidine suppresses ethyl pyruvate decomposition upon adsorption on Pt [16]. Surface science studies indicate that 1-(1-naphthyl)ethylamine [23] and benzene [24] thermally stabilize methyl pyruvate against decomposition on Pt(1 1 1) [23]. Hydrogen may limit the extent of substrate polymerisation [18].

Acetic acid plays a central role in the enantioselective hydrogenation of activated ketones over Pt/Al₂O₃. It is to date the best solvent for the hydrogenation of a number of substrates affording over 95% e.e. [25–27]. Besides its role as a solvent, acetic acid clearly affects the conformational behaviour of the chiral cinchona modifier in solution [28,29] and forms ionic complexes with the modifier upon protonation of the basic N-atom(s) [30], which are proposed to be involved in the catalytic cycle [31]. Additionally, acetic acid adsorbs on Al₂O₃ preventing adsorption of the chiral modifier on the support [32]. Formation of oxonium compounds (O⁺[Al(OAc)₂]₃) has also been reported as a result of alumina dissolution in the presence of acetic acid which was proposed to affect the reaction mechanism in acidic media [21,33].

Here, we investigated the undesired side reactions of ethyl pyruvate during the enantioselective hydrogenation on Pt/Al₂O₃ using *in situ* attenuated total reflection infrared (ATR-IR) spectroscopy in combination with *ex situ* diffuse reflectance infrared (DRIFT) spectroscopy and pulse thermal analysis. We show that the alumina support is active in catalysing ethyl pyruvate degradation by aldol-type condensation and that this reaction and the platinum-catalysed decomposition/polymerisation are suppressed in the presence of acetic acid as solvent.

2. Experimental

2.1. Materials

Ethyl pyruvate (EP, Fluka, >98%) and acetic acid (Fluka, 99.8%) were used as received. EP was also used after distillation in vacuum and stored at 4 °C. Dichloromethane solvent (Baker, 99.5%) was stored over 5A molecular sieves. Toluene (Baker, 99.5%) was dried over Na. Nitrogen and hydrogen gases (99.999 vol.%) were supplied by PanGas. The 5 wt.% Pt/Al₂O₃ (E4759) was purchased from Engelhard. Al₂O₃ (Fluka, for chromatography) was used as reference for the catalyst support.

2.2. ATR-IR spectroscopy

Pt/Al₂O₃ particulate coatings were obtained by dropping a suspension of the unreduced catalyst in water (ca. 25 mg/ml_{water}) over a ZnSe internal reflection element (IRE, 45°, 52 mm × 20 mm × 2 mm, Komlas). The suspension was then dried in air at ambient temperature. The Pt/Al₂O₃ coating was

reduced in flowing H₂ at 350 °C for 2 h in a quartz tube reactor. The temperature was kept lower than that typical for catalyst reduction (400 °C) to avoid damage of the ZnSe material. After cooling to ambient temperature, the coated IRE was transferred to the ATR-IR cell. Pt/Al₂O₃ model films were obtained by electron beam physical vapour deposition of Al₂O₃ (film thickness: 100 nm) and Pt (1 nm) materials onto a Ge IRE (45°, 52 mm × 20 mm × 2 mm, Komlas) as reported in detail elsewhere [34]. After mounting, the ATR-IR cell was placed on a commercial mirror setting (Specac) within the sample chamber of the spectrometer, which was purged with dry air to minimize absorption of atmospheric water vapour and CO₂. Irrespective to the coating preparation, ATR-IR measurements were performed at 15 °C by pumping CH₂Cl₂ solutions saturated with gases (N₂ and H₂) across the coated IRE. Before admission of adsorbate solutions, the Pt surface was reduced *in situ* with H₂-saturated CH₂Cl₂ [34]. The procedure used for the ATR-IR measurements implies that experiments are carried out under conditions of hydrogen diffusion limitation owing to the low hydrogen concentration.

Spectra were collected with a Bruker Optics IFS 66 infrared spectrometer equipped with a MCT detector by co-adding 200 scans at 4 cm⁻¹ resolution and are presented as difference spectra in the form of $A = -\log I/I_0$.

2.3. Catalytic hydrogenations

Hydrogenation reactions were carried out in a magnetically stirred stainless steel autoclave (50 ml) controlled by a computerised constant-volume constant-pressure equipment (Büchi BPC 9901). The 5 wt.% Pt/Al₂O₃ catalyst was pre-reduced before use in a fixed-bed reactor by flushing with N₂ at 400 °C for 30 min, followed by reductive treatment in H₂ for 60 min at the same temperature. After cooling to room temperature in H₂, the catalyst was immediately used for hydrogenation. According to standard conditions 42 mg catalyst, 1.84 mmol substrate, and 5 ml solvent were stirred (1250 rpm) at 1 or 10 bar for 1 h at 15 °C. For enantioselective hydrogenations 6.8 μmol of the modifier were used.

For DRIFT measurements the catalyst was separated from the reaction solution by filtration, washed with the solvent and dried under air. Deviations from the standard conditions (addition of small amounts of acetic acid) are specified in the text. Conversion and enantiomeric excess (e.e. (%)) = $100 \times |(R - S)/(R + S)|$ were determined by GC using a Chirasil-DEX CB column (Chrompack).

2.4. DRIFT and pulse thermal analysis

Fresh and used catalysts recovered after catalytic hydrogenations of EP were analyzed by diffuse reflectance infrared spectroscopy (DRIFTS) and pulse thermal analysis (PulseTA[®]). For DRIFTS, samples were measured diluted in KBr at 25 °C using a commercial cell (Harrick) and by co-adding 200 scans at 4 cm⁻¹ resolution.

Thermogravimetry (TG) combined with mass spectrometry (MS) was carried out on a Netzsch STA 409 thermoanalyser

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