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Effect of achiral condensed aromatic additives on the enantioselective hydrogenation of ethyl pyruvate over cinchonidine-platinum catalysts

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Abstract

The effect of the addition of various nitrogen containing and condensed aromatic compounds on both the rate and the enantioselectivity in the hydrogenation of over supported cinchonidine-Pt catalysts has been investigated. The results show that preadsorbed quinoline and acridine cannot be fully replaced from the surface of platinum by cinchonidine. It has been found that the addition of these compounds increases both the reaction rate and the enantioselectivity (both ee max and ee end values). The observation that these additives have no negative effect on the enantioselectivity indicates that generally accepted mechanistic models need some corrections.

Keywords: Enantioselective hydrogenation; Ethyl pyruvate; Cinchonidine; Supported platinum catalysts; Achiral additives; Quinoline; Acridine; Competitive adsorption

1. Introduction

Hydrogenation of ethyl pyruvate over supported cinchonidine-Pt catalyst system is the most frequently studied heterogeneous catalytic enantioselective hydrogenation reaction [1–3]. There is a general view that in the enantiodifferentiation step the modifier forms a 1:1 complex with the substrate molecule. In generally accepted "*surface model*" it has been proposed that enantiodifferentiation takes place at the Pt surface at "chirally modified" sites [4,5]. Contrary to that the "*shielding effect model*" suggests that in the enantiodifferentiation step the substrate-modifier complex formed in the liquid phase is involved [6,7].

In the hydrogenation of ethyl pyruvate over supported Pt catalysts in the presence of cinchonidine definite rate acceleration and high ee values (above 80%) were observed [8,9]. The addition of achiral tertiary amines resulted in further increase in the ee values at low concentration (10^{-5} M) of cinchonidine [10]. Similar effect of achiral compounds has been observed in homogeneous catalysis, e.g. catalyst based on a combination of a chiral and an achiral monodentate ligand leads to a higher enantioselectivity compared to the corresponding homo-complexes in asymmetric C–C bond formation [11]. However, mixtures of chiral and achiral monodentate ligands in asymmetric Rh-catalyzed olefin hydrogenation resulted in reversal of enantioselectivity [12].

Cinchonidine has two key structural elements, i.e., the condensed quinoline ring and the large quinuclidine moiety containing a tertiary nitrogen atom. The replacement of quinoline ring for a phenyl or pyridyl one resulted in complete loss of enantiodifferentiation ability [13]. The "*surface model*" assumes that cinchonidine adsorbs onto Pt by its aromatic quinoline ring [14]. Consequently, the condensed π-system has been considered as the anchoring site of cinchonidine. The smaller the size of this anchoring site the lower the strength of adsorption of the chiral modifier,

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what results in decreased enantioselectivity. In the ''shielding effect'' model the quinoline ring is responsible for the chemical shielding leading to enantiodifferentiation as described earlier [6]. The decrease of the size of the aromatic ring will cause loss of shielding effect as it has been evidenced in different organic reactions [15,16].

Similar losses in the enantiodifferentiation ability were observed upon using derivatives of cinchonidine with full or partial hydrogenation of the quinoline ring [17,18]. These results were explained either by the decrease of the strength of adsorption of the ring-saturated compounds [19] or the diminished shielding exerted by the hydrogenated ring systems [6].

In enantioselective hydrogenation of α-ketoesters the loss of modifier, due to its ring hydrogenation, was observed at low concentration of cinchonidine (10^{-6}–10^{-5} M) and at prolonged reaction time [20,21]. This fact is considered as indirect evidence that cinchona alkaloids interact with the Pt surface via their quinoline ring.

With respect to the validity of surface model various indirect spectroscopic evidences were found. Depending on the surface coverage cinchonidine adsorbs in three different forms on Pt [22,23]. At low concentration of cinchonidine the flat adsorption mode prevails, while upon increasing the coverage (10^{-4}–10^{-3} M) two other species, the α-H abstracted and the N lone pair bonded cinchonidine molecules have been observed [24]. It has been suggested that the flat adsorption mode is involved in the formation of chirally modified sites, while all others are considered as ''spectators''.

It has been found that over Pt(1 1 1) at 300 K quinoline forms an essentially immobile monolayer and it preferentially adsorbs in a lying-down configuration via the aromatic π-system [25]. In a recent study the adsorption of quinoline and cinchonidine has been investigated [26]. It was concluded that (i) both molecules are bound through the π-system, and (ii) ''the possibility of a displacement of the (chiral) modifier by adsorbed educts ... has to be taken into account''.

Different amines including quinoline were used as additives in racemic hydrogenation of methyl pyruvate [27,28]. The addition of quinoline resulted in a definite rate acceleration [28] by a factor of 2. In another study the effect of nitrogen bases, such as quinoline, triethylamine and pyridine was investigated [29]. The dependencies of the reaction rate and the ee values of the quinoline concentration had completely different character. The rate passed through a very sharp maximum at very low concentration of quinoline followed by a fast decay after the maximum, while the ee passed through a very slight maximum (from 84% to 88%) and decreased relatively slowly to 79% after 10-fold increase of quinoline.

Quinoline was used as an additive in liquid-phase hydrogenation of acetylene [30] and 1-hexene, cyclohexene [31]. The addition of quinoline decreased the rate of hydrogenation of both alkenes, but even in excess quinoline the residual activity of the catalyst was above 50%. It was suggested that the weakly bound quinoline is displaced by the alkenes and the hydrogenation proceeded over this part of platinum surface [31].

Based on this finding we suggest if condition of competitive adsorption between cinchonidine and condensed aromatic compounds can be established, the number of ''chirally modified sites'' should decrease resulting in definite loss of enantioselectivity. Consequently, in this way the validity of ''surface model'' can be tested.

The aim of this study is to demonstrate how the addition of different condensed aromatic compounds will alter the kinetic patterns in the enantioselective hydrogenation of ethyl pyruvate over two different supported Pt catalysts at low concentration of cinchonidine.

2. Experimental part

2.1. Hydrogenation of ethyl pyruvate

The hydrogenation was carried out as described earlier [32]. 2.7 wt.% Pt/SiO_2 (H/Pt = 0.67, CO/Pt = 0.85) and commercial 5% Pt/Al_2O_3 (Engelhard 4759, H/Pt = 0.27), catalysts were used. Toluene (Reanal) was used as a solvent. Ethyl pyruvate (Fluka) was freshly distilled before each catalytic experiment. Acridine, cinchonidine, were purchased from Fluka and used as received. Quinoline (Reanal) was distilled before use. Naphthalene and anthracene were purchased from Aldrich and were used as received. The hydrogenation was carried out in a 300 cm^3 SS-autoclave: $[\text{ethyl pyruvate}]_0 = 1.0$ M, $P_{H_2} = 50$ bar, solvent: toluene, stirring rate 500 rpm, reaction temperature: 20 °C. Both injection and premixing techniques were used to introduce the chiral modifier and achiral additives [9]. In preliminary results the main components, i.e., cinchonidine and the additives were introduced either by separate injection (Inj-I), coinjection (Inj-II), separate premix (Pr-I) and copremix (Pr-II) Based on preliminary experiments quinoline was premixed and cinchonidine was injetcted at $t = 0$ in all further runs. Prior to the hydrogenation all catalysts were reduced in hydrogen for 90 min at 400 and 300 °C, for Al_2O_3 and SiO_2 supported catalysts, respectively.

2.2. Analysis

Samples were analysed by a GC using a capillary column (Supelco BETA-DEX™ 225, 0.25 mm, 30 m) and flame ionisation detector. The enantioselectivity is expressed as $ee = ([R - S]/[R + S])$.

2.3. Abbreviations

The ee_{max} means the highest enantiomeric excess value measured in a given reaction. The ee_{end} values were measured after 90 min. The ee values in the ee-conversion dependencies had a relative error in the range of 5%, with completely reproducible shapes.