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Identification of catalyst surface species during asymmetric platinum-catalysed hydrogenation in a “supercritical” solvent†

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In situ **attenuated total reflection infrared spectroscopy studies during the enantioselective hydrogenation of ethyl pyruvate in “supercritical” ethane over a chirally modified Pt/Al_2O_3 catalyst show the preferential adsorption of ethyl pyruvate as *cis*-conformer and indicate a hydrogen bond interaction of this species with the co-adsorbed modifier cinchonidine.**

Asymmetric catalysis is one of the most elegant strategies for synthesising optically active compounds.[1] The majority of enantioselective catalytic reactions are homogeneously catalysed by transition metal complexes with chiral ligands. However, for industrial processes heterogeneous catalysts are preferred because they can be more easily separated and reused. One of the most promising asymmetric heterogeneous catalytic systems is *Cinchona* alkaloid-modified platinum used for enantioselective hydrogenation of carbonyl functions, discovered in 1979.[2] A prominent model reaction for this system is the hydrogenation of ethyl pyruvate (EP) to ethyl lactate (EL).[3]

Despite the remarkable progress achieved in understanding the mechanism of enantiodifferentiation, little is known on the adsorption states of reactants and modifier during reaction.[3,4] Various spectroscopic methods were applied to investigate either substrate[5] or modifier[6] adsorption on catalytically active surfaces. However, in these studies the experimental conditions were generally far from those during the catalytic reactions, or model catalysts were used. Recently, we have studied the interaction of ketopantolactone with cinchonidine modified Pt/Al_2O_3 thin films in hydrogen saturated CH_2Cl_2 by attenuated total reflection (ATR) IR modulation spectroscopy.[7] An important step forward is the use of a real catalyst instead of a model catalyst and the application of *in situ* spectroscopy.

“Supercritical” fluids as solvents for hydrogenation reactions have received considerable interest in the last decade due to their unique properties.[8] With this in mind we studied the enantioselective ethyl pyruvate hydrogenation over a commercial 5% Pt/Al_2O_3 catalyst chirally modified by cinchonidine (CD) in “supercritical” ethane (scC_2H_6),‡ which was previously used as solvent for EP hydrogenation.[9] To be able to investigate the catalyst under reaction conditions, a new high-pressure spectroscopy cell was employed, which allows the combination of phase behaviour studies with FTIR investigations.[10] The phase behaviour observations ensured that the reaction mixture was present as a single phase during the spectroscopic studies. FTIR studies were simultaneously performed on both the “supercritical” fluid phase by transmission measurements (*i.e.* to follow the reaction progress) and on the catalytically active solid surface by ATR measurements.

Fig. 1a shows a comparison of IR spectra of liquid EP, liquid EL and a 1 : 1 mixture of both dissolved in “supercritical” ethane (*i.e.* at 50% conversion of the hydrogenation reaction). The carbonyl stretching band of EP at 1729 cm^{-1} shows a shoulder at 1753 cm^{-1} which can be traced back to the *trans* and *cis* conformation, respectively.[11] Due to the low polarity of scC_2H_6, upon dissolution the bands are shifted to 1742 cm^{-1} and 1768 cm^{-1}, respectively. The intense ethane signal covers the 1350 to 1600 cm^{-1} region. The characteristic bands of the reactant and product at 1302 and 1221 cm^{-1} (carboxyl-carbon vibration, for EL coupled with a hydroxyl bending mode), respectively, can be used to follow the reaction (*cf.* ESI† and ref. 10). Model calculations using harmonic frequency analysis revealed that both bands belong to the *trans* conformation of the EP and EL species.† The bands of the *cis* conformers appear both around 1260 cm^{-1}. The intensity of the vibrational band at 1136 cm^{-1} associated with carbonyl-carbon vibrations (alcoholic-carbon for EL, appearing at 1127 cm^{-1}) does not change significantly. The two bands of EL at 1047 and 1019 cm^{-1} and the band of EP at 1021 cm^{-1} merge into one smaller signal at 1027 cm^{-1} with a shoulder at 1040 cm^{-1}.

Before studying the hydrogenation reaction, preliminary experiments with EP in scC_2H_6 using Al_2O_3 and CD-premodified Pt-black were conducted. The resulting ATR-IR spectra are shown in Fig. 1b, spectra 1 and 2, respectively.

Compared to the spectra in Fig. 1a, the carbonyl stretching band around 1740 cm^{-1} is broadened, and the shoulder at higher wavenumbers is more pronounced. Especially on platinum, the

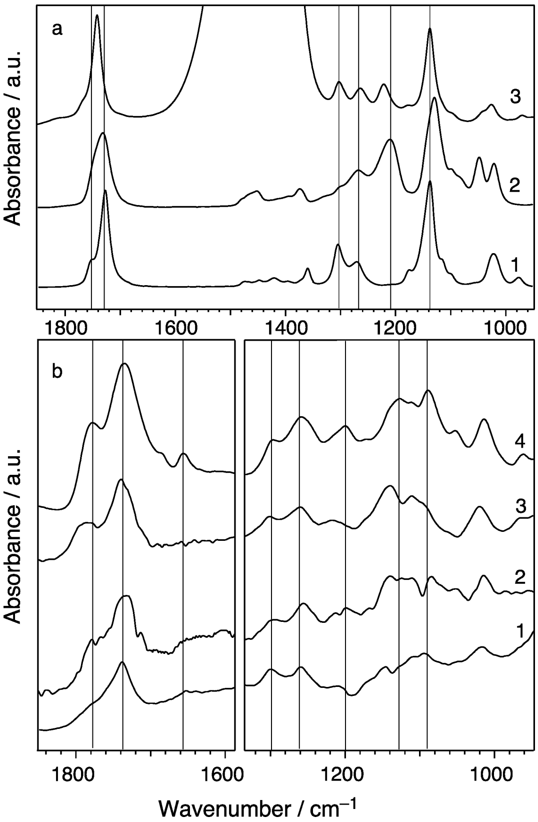

Fig. 1 a) FTIR spectra of (1) pure liquid EP, (2) pure liquid EL, and (3) a 1 : 1 mixture of EP and EL in “supercritical” ethane at 40 °C and 95 bar. b) ATR-IR spectra of adsorption/reaction of EP in “supercritical” ethane on (1) Al_2O_3 in absence of H_2; (2) CD-premodified Pt-black; (3) unmodified Pt/Al_2O_3, but CD dissolved in EP; (4) CD-premodified Pt/Al_2O_3. Conditions in all experiments were 40 °C, and 95 bar. Molar ratio EP : H_2 : ethane = 1 : 5 : 200.‡

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† Electronic supplementary information (ESI) available: figure with transmission spectra at different reaction times to follow the reaction progress and details of the model calculations. See http://www.rsc.org/suppdata/cc/b3/b315591a/

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relative intensity of the bands around 1300 and 1260 cm^{-1} is shifted to the latter one. Both results indicate a shift of the *cis/trans* equilibrium from the *trans* to the *cis* conformer, as was similarly reported for methyl pyruvate (MP) on Ni(111) under vacuum and at low temperatures.[5a] The intense signal at 1136 cm^{-1} is composed of several overlapping bands in the range of 1090 to 1150 cm^{-1}, suggesting that EP can adsorb on the surface in several ways and tilt angles.

Spectra 3 and 4 in Fig. 1b depict the *in situ* ATR-IR spectra of two different hydrogenation experiments using the Pt/Al_2O_3 catalyst. In experiment 3, the chiral modifier cinchonidine (CD) was premixed with EP, and the catalyst was suspended in pure i-PrOH. In experiment 4, pure EP was introduced into the reactor, but the catalyst was suspended in a CD containing i-PrOH solution. None of the spectra 2, 3 and 4 shows signals of CD, but for different reasons: in experiment 3 no CD is present on the surface, in experiment 2 and 4 CD is already accounted for in the subtracted background spectrum. Both experiments, 3 and 4 showed a conversion around 50% after 2 h, but only experiment 4 revealed an enantiomeric excess (ee) towards the *R*-EL of 39%. The lower ee compared to previous studies[9] may be attributed to the unfavorable mass transport situation compared to slurry or fixed bed reactors. The product of experiment 3 was racemic. The absence of ee can be explained by the very low solubility of CD in scC_2H_6, as it has been shown recently that the point in time of modification of the catalyst (premodification *vs. in situ*) has no influence on ee.[12] Almost no CD is transported to the catalyst locally fixed on the internal reflection element, therefore no enantiodifferentiation can take place. These results underline the necessity of combining *in situ* spectroscopic data with catalytic results to ensure correct interpretation of the data.

A comparison of the spectra 2, 3 and 4 in Fig. 1b reveals a band around 1660 cm^{-1}, as well as two smaller signals at 1710 and 1050 cm^{-1} only present in spectrum 2 and 4. As the catalytic results of experiment 3 gave no ee (and therefore no substrate–modifier interaction on the surface), these signals can be assigned to interactions between the chiral modifier (CD) and the substrate (EP) on platinum. Especially the 1660 cm^{-1} band may be attributed to carbonyl stretching vibrations of EP, shifted to lower wavenumbers due to hydrogen bonding between the quinuclidine nitrogen and the keto-oxygen atom of EP. This interpretation is in line with our recently reported study on ketopantolactone adsorption on a CD-modified Pt/Al_2O_3 thin film.[7]

In both spectra, 3 and 4, the shoulder at 1780 cm^{-1} is significantly stronger compared to the spectrum measured for the bulk fluid phase, and the relative intensity of the bands at 1302, 1260 and 1200 cm^{-1} is shifted to the band at 1260 cm^{-1}. Hence the *cis/trans* equilibrium of EP, dominated by the *trans* species in apolar solvents, is shifted towards the *cis* conformer upon adsorption on Pt. This result is in accordance with predictions of DFT model calculations of EP adsorption on Pt metal clusters.† The knowledge gained leads to the proposition of a diastereomeric *cis*-EP–CD complex as depicted in Fig. 2. Such a complex is also supported by earlier *ab initio* calculations predicting that both *trans*- and *cis*-EP may form a diastereomeric enantiodifferentiating complex with CD.[13] Which of these complexes is finally crucial for enantiodifferentiation cannot be decided based on this study because the most abundant surface species must not necessarily be the kinetically most significant.

Our study shows that the catalytic solid–fluid interface of a technical catalyst can be studied during asymmetric hydrogenation in "supercritical" ethane. To our knowledge it represents the first *in situ* study of a solid-catalysed asymmetric reaction.[8] The measurements give experimental evidence for model calculations predicting that *cis*-EP is the more stable conformer on a Pt surface. Furthermore, the study confirms the important role of hydrogen bonding in the substrate–modifier interaction uncovered previously on a thin film model catalyst.[7]

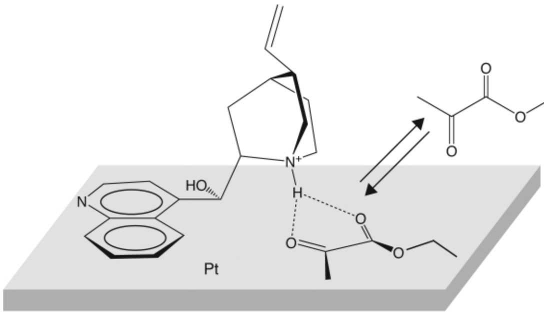

Fig. 2 Proposed model for EP adsorption during enantioselective hydrogenation in scC_2H_6 over Pt/Al_2O_3 chirally modified by CD. The co-adsorbed species interact *via* hydrogen bonding, forming a diastereomeric complex.

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Notes and references

‡ *Experimental*: The Pt/Al_2O_3 catalyst (Engelhard 4759) was first pretreated at 400 °C in hydrogen, then stirred in an i-PrOH solution of cinchonidine (Fluka). The suspension was transferred onto the ZnSe internal reflection element (IRE, Komlas GmbH, Berlin) and dried under vacuum.

The coated IRE was mounted into the cell and after flushing the *in situ* cell with nitrogen, background spectra were measured. Subsequently, 0.2 g EP (Fluka) was introduced into the cell, which was preheated to 40 °C, avoiding contact with the catalyst. Ethane and hydrogen were added, resulting in a molar ratio EP : H_2 : ethane = 1 : 5 : 200. The reaction mixture was stirred vigorously, and spectra were taken in regular time intervals.

Safety note: The experiments described in this paper involve the use of relatively high pressure and require equipment with the appropriate pressure rating.

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