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Chiral modification of platinum catalysts by cinchonidine adsorption studied by *in situ* ATR-IR spectroscopy

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Adsorption of cinchonidine on a platinum model catalyst studied by *in situ* ATR-IR spectroscopy revealed that the adsorption mode depends on surface coverage and is affected by concomitant adsorption and fragmentation of solvent molecules.

Heterogeneous asymmetric hydrogenation on chirally modified catalysts is a promising route for producing chiral molecules with high optical purity from prochiral reactants. At present, tartaric acid modified Ni catalysts[1,2] and cinchona modified Pt based catalysts[3–5] are the most successful systems for the hydrogenation of β-keto esters and α-keto esters, respectively. With respect to the latter, the adsorption mode of cinchonidine (CD) is a critical factor, and still a matter of debate. Direct spectroscopic information is available only from earlier XPS and LEED[6] and recent NEXAFS[7] studies of the adsorption of 10,11-dihydrocinchonidine on Pt(111) under UHV conditions. At 298 K the quinoline ring was found to lie almost parallel to the metal surface, whereas a tilting angle of *ca.* 60° was found at 323 K. However, these studies fail to describe the adsorption under reaction conditions, *i.e.* in the presence of both the solvent and H_2. With the present work we aim at closing this gap by studying the adsorption of CD using attenuated total reflection IR spectroscopy (ATR-IRS)[8] close to reaction conditions. For this purpose we have developed a model system based on a Pt/Al_2O_3 coated Ge internal reflection element.[9] In the following it will be shown that the presence of a solvent acting as a competing adsorbate is a crucial factor for modifier adsorption. Adsorption of CD on Pt/Al_2O_3 turns out to be complex. Several adsorption modes of CD can be distinguished, depending on coverage and time similar to recent findings for the Ni–tartrate system.[10]

ATR spectra of cinchonidine (CD) adsorbed from H_2-saturated CH_2Cl_2 solvent on Pt/Al_2O_3 are shown in Fig. 1.† Before recording the ATR spectra the Pt/Al_2O_3 film was treated with hydrogen saturated CH_2Cl_2 which results in a cleaning of the Pt.[9] After this the background spectrum was recorded. Upon admitting a H_2-saturated solution of CD to the sample positive and negative signals were immediately observed in the ATR spectra. The positive signals arise from molecules, which are added to, negative signals from molecules, which are removed from the interface, with respect to the reference spectrum. We assign the positive signals to adsorbed CD, whereas the negative signals are due to simultaneous removal of adsorbed solvent decomposition products as well as the displacement of solvent from near the interface, as detailed below. The spectra exhibit distinct concentration [compare Fig. 1(a) and (c)] and time dependence [Fig. 1 (b) and (e)] and are clearly different from the solution spectrum as a consequence of the interaction of CD with the Pt/Al_2O_3. By contacting quinoline (Q, not shown) with Pt/Al_2O_3, the same concentration and time behaviour of the corresponding vibrational bands was observed, indicating that the interaction of CD with the surface is dominated by the quinoline moiety. The change of the relative intensity of the vibrational bands with concentration and time and the appearance of new bands with respect to the solution spectrum can arise due to (i) a chemical reaction of CD or (ii) a change in adsorption geometry. Feasible chemical reactions of the quinoline moiety under the applied conditions are hydrogenation and α-H abstraction. As concerns hydrogenation, several possible hydrogenation products (1,2,3,4- and 5,6,7,8-tetrahydroquinoline and decahydroquinoline) were adsorbed from CH_2Cl_2 on the Pt/Al_2O_3 film. Although for most of them adsorption could be observed, none of them exhibited the vibrational bands shown in Fig. 1 and hence we exclude adsorbed hydrogenation products as the origin of the bands in Fig. 1. To our knowledge no analysis of the vibrational spectrum of quinoline (intact and/or after α-H abstraction) on Pt has been reported so far. On the other hand for the chemically related pyridine on Pt detailed analysis exists.[11] Intact pyridine and pyridine after α-H abstraction can clearly be distinguished. After adsorption of pyridine from hydrogen-saturated CH_2Cl_2 we predominantly observed the bands which have been associated with intact pyridine in a tilted orientation and bound *via* the N-atom.[11] Although α-H abstraction is feasible, we conclude that it is not a dominant process under the applied conditions. On the other hand the absence of the signal at 1635 cm^{-1} corresponding to $\nu(C{=}C)$ of the vinyl moiety indicates that CD is hydrogenated at this site.

Based on the above mentioned results we conclude that the observed positive bands are mainly associated with chemically intact CD and that the changes in relative intensity of the bands in Fig. 1 are associated with changes in adsorption geometry. At

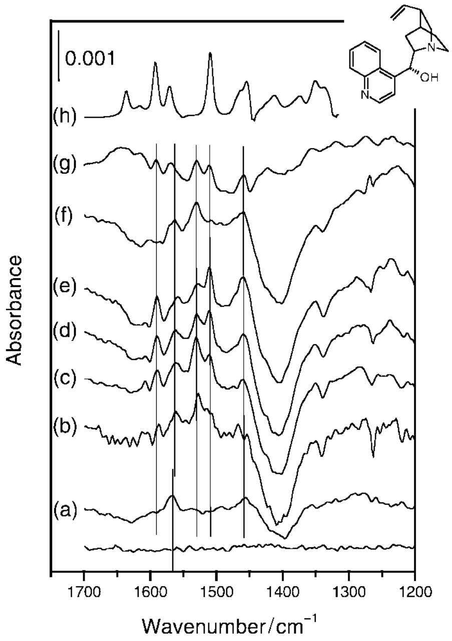

Fig. 1 ATR-IR spectra of cinchonidine adsorption on Pt/Al_2O_3 at 283 K from (a) 10^{-7} mol l^{-1} and (b)–(e) 10^{-3} mol l^{-1} solution in CH_2Cl_2 (recorded after 2, 3, 42 and 122 min, respectively), (f) followed by neat solvent flow; (g) from a 10^{-4} mol l^{-1} solution in cyclohexane at 293 K; (h) scaled (1 : 80) transmission spectrum of cinchonidine in CH_2Cl_2.

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least three different adsorption geometries of CD (in the following termed ‘species’) can be distinguished by analysing the spectral region between 1500 and 1650 cm^{-1}, associated with the quinoline ring vibrations. A first species associated with only one band in this region at 1567 cm^{-1} predominates at 10^{-7}–10^{-6} mol l^{-1} [Fig. 1(a)]. At higher solution concentration, signals at 1610, 1590, 1567, 1530, 1511 and 1460 cm^{-1} are observed, having relative intensities changing with adsorption time. A slight red-shift is observed for the signal at around 1570 cm^{-1} upon increasing the concentration above 10^{-6} mol l^{-1} together with the appearance of the signal at 1530 cm^{-1}. The features at 1530 and 1567 cm^{-1} dominate the spectrum: (i) when slowly increasing the concentration of CD from 10^{-7} to 10^{-5} mol l^{-1}, (ii) at the very first stages of adsorption when flowing higher concentration ($>10^{-5}$ mol l^{-1}) of CD [Fig. 1(b)], and (iii) when flowing neat solvent after saturating the sample [Fig. 1(f)]. They are attributed to a second species that is therefore strongly adsorbed. A third species is associated with strong bands at 1511 and 1590 cm^{-1} with a spectrum resembling that of CD in solution [Fig. 1(h)]. This species appears only at later stages of adsorption and at high concentration [Fig. 1(c)–(e)] and disappears when flowing neat solvent. This species is therefore only weakly bound, which is in line with the fact that its spectrum very much resembles the (unperturbed) solution spectrum. Interestingly, the intensity of the bands associated with the second and third species are anticorrelated, which is best seen by comparing the signals at 1511 and 1530 cm^{-1} in Fig. 1(b)–(e). Such behaviour is consistent with mutually interconverting species, the driving force for this process being the solution concentration. The signal at 1460 cm^{-1} observed for all three species is associated with the quinuclidine moiety of CD as the adsorption of quinuclidine (QD) on Pt/Al_2O_3 clearly indicated (not shown).

Knowledge of the direction of the dynamic dipole moment of a selection of vibrations (from *ab initio* calculations) combined with the metal surface selection rule[12] allows information to be gained about the local adsorbate orientation. Fig. 2 shows that the vibration at 1509 cm^{-1} in the solution spectrum is polarised roughly along the long axis of the quinoline moiety, whereas the mode at 1570 cm^{-1} is polarised perpendicular to it.

In line with the calculated polarisation of the bands, the following interpretation of the spectra can be given: the species associated with only one strong signal at 1567 cm^{-1} has the long axis of the quinoline moiety nearly parallel to the surface with a degree of tilting of the short axis, probably induced by the quinoline-N and the O–H group. For the second species the appearance of a second band at 1530 cm^{-1} indicates a change in orientation. We tentatively assign the band at 1530 cm^{-1} to the 1509 cm^{-1} band in solution, which is blue-shifted due to an interaction with the surface. A similar blue-shift of the corresponding bands was observed for pyridine on Pt adsorbed through the N atom in a tilted orientation.[11,13] The pyridine spectrum recorded in the presence of H_2 and CH_2Cl_2 shows bands with A_1 and B_1 symmetry,[11] indicating that none of the molecular axes are oriented parallel to the surface. Hence, the observed blue-shift of the 1530 cm^{-1} band, in analogy with adsorbed pyridine under our conditions, and the calculated polarisation of the 1530 cm^{-1} band are consistent with the interpretation that for the second species the long axis of the quinoline moiety is no longer parallel to the surface. The weakly bound third species does not show significant orientation preferences.

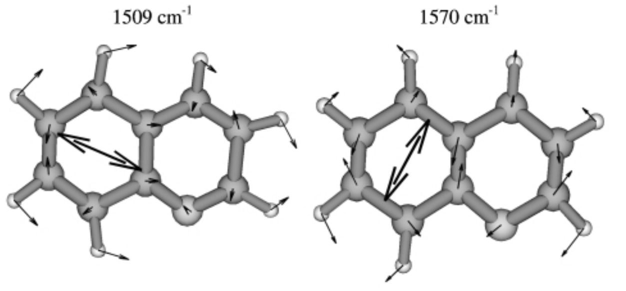

Fig. 2 Schematic of two of the vibrational modes of quinoline used to identify adsorption orientation. Arrows indicate atomic displacement vectors and the direction of the dynamic dipole moment, respectively. The corresponding experimental IR frequencies for cinchonidine in CH_2Cl_2 are also given.

As a general trend the quinoline moiety of CD is tilted more with increasing solution concentration and coverage. This is consistent with an increase of the average thickness of the adsorbate layer (defined as the distance between the Pt/adsorbate and the adsorbate/solution interfaces) and thus the displacement of solvent from very near the interface. This effect is directly observed in the ATR spectra. The negative peak at 1260 cm^{-1} corresponds to the strongest solvent vibration. Upon adsorption of CD (increasing the thickness of the adsorbate layer) this peak becomes negative, since, with respect to the reference spectrum, less solvent is probed by the electromagnetic field. The other negative signals at around 1635, 1400, 1338 and 1120 cm^{-1} (not shown) are associated with removal of water, CH_x and ethylidyne (CCH_3), respectively, from the adsorbate layer. CH_x fragments (1400 cm^{-1}) are formed from CH_2Cl_2 decomposition.[14] Upon admission of a solution of CH_2Cl_2 in cyclohexane on the Pt/Al_2O_3 sample the band was also observed supporting this view. Ethylidyne (1338, 1120 cm^{-1}) is likely formed by recombination of CH_x fragments, which is supported by the observed evolution of ethene on Pt/Al_2O_3 in contact with CH_2Cl_2.[14] CD adsorption from cyclohexane solvent afforded the same positive signals associated with CD, but not the negative signals associated to CH_x fragments and ethylidyne [Fig. 1(g)].

The ATR spectra clearly show that the adsorption mode of CD is coverage dependent and that CD competes with solvent decomposition products for adsorption sites. This observation adds an important new facet to the interpretation of the ‘solvent effect’ in enantioselective hydrogenation over cinchona-modified platinum.

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Notes and references

† *In situ* experiments were carried out with a home-made stainless steel flow through cell by recording spectra at 283 K and co-adding 200 scans at 4 cm^{-1} resolution with a Bruker IFS/66 spectrometer equipped with a liquid-N_2-cooled MCT detector. Adsorption was carried out from H_2-saturated millimolar solutions in CH_2Cl_2 solvent (if not otherwise specified) after cleaning of the metal surface with H_2-saturated solvent. ATR spectra are presented in absorbance units with the last spectrum recorded during H_2-cleaning serving as reference. Pt/Al_2O_3 model films were prepared as described elsewhere.[9] Density functional theory (B3PW91 / cc-pvtz) was used to calculate frequencies and determine the dynamic dipole moment of each vibration.

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