J. Am. Chem. Soc. **2001,** *123,* 11115−11116 11115

Adsorption Geometry of Modifiers as Key in Imparting Chirality to Platinum Catalysts

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Received July 27, 2001

Chirality is prominent in the biochemistry of living organisms, since nature has evolved to favor one handedness over the other. The use of the wrong enantiomer in pharmaceutical applications can be deadly: witness the case of thalidomide, where the analgesic properties of one enantiomer is offset by the fetal malformations caused by the other.[1] At present, the best way to synthesize enantiomerically pure chemicals is via homogeneous catalysis.[2] However, since such processes often require expensive and hard-to-handle metal complexes which are difficult to separate from the products, the use of heterogeneous catalysts is much preferred. The most promising route for that is via the addition of chiral modifiers to regular catalysts,[3] but such approach has so far been limited by the lack of understanding of the corresponding surface processes.[4] One of the few successful examples of chiral-modified heterogeneous catalysis is the hydrogenation of α-ketoesters on supported platinum catalysts modified with cinchona alkaloids.[5−8] Unfortunately, tuning that process for specific applications is hampered by the fact that small changes in structure[6−9] or concentration[8−10] of the modifier, particle size of the metal catalyst,[11] nature of the solvent,[6−9] and reaction conditions[12] all affect its activity and selectivity in unpredictable ways. Here we report on results from in situ reflection−absorption infrared spectroscopy (RAIRS) studies on the adsorption of cinchona from solution onto platinum surfaces, which shed some light on the reasons for those changes.

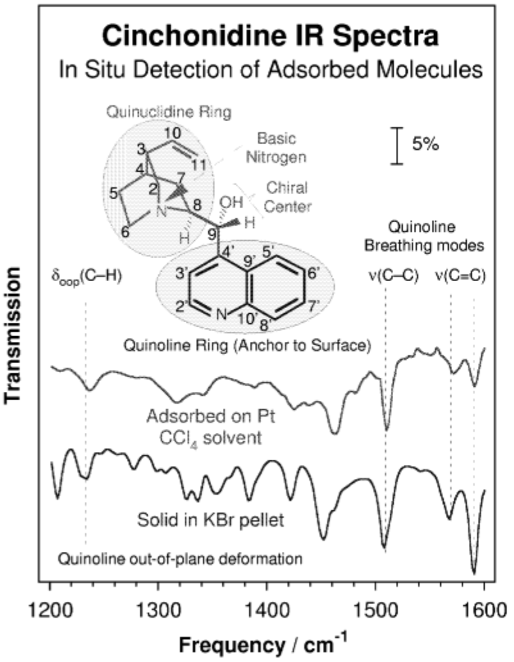

Figure 1. Infrared spectra for cinchonidine, pure (bottom), and adsorbed from a carbon tetrachloride solution onto a platinum foil (top). A comparison of the two spectra points to the specific changes induced by the interaction of this modifier with the platinum surface. In particular, the main quinoline in-plane deformation modes around 1591, 1568, and 1507 cm^{-1} are all retained, but an increase in relative importance of the peak at 1462 cm^{-1} compared to the signal at 1452 cm^{-1} is seen. This means that cinchonidine remains molecular upon adsorption but that both quinoline and quinuclidine rings adopt well-defined orientations on the surface. In addition, the blue shift of the C−H deformation mode around 1230 cm^{-1} indicates some rehybridization due to a strong interaction of the aromatic moiety with the metal. Inset: Schematic representation of the molecular structure of the cinchonidine.

The adsorption characteristics of chemisorbed cinchona are illustrated by the vibrational data provided in Figure 1, which compares the in situ RAIRS trace obtained during exposure of a platinum surface to a saturated (6.8 mM) solution of cinchonidine in carbon tetrachloride against a spectrum from the pure alkaloid. The structure of cinchonidine is provided in the inset of that figure to highlight the three functional parts that have been identified in these modifiers, namely: (1) the anchoring quinoline aromatic ring, the moiety believed to be responsible for adsorption to the metal, (2) the tertiary quinuclidine ring, an amine group with a basic nitrogen atom which facilitates complexation with the reactant, and (3) the stereogenic region around the C_8 and C_9 carbon atoms responsible for the chirality of the product.[7] The choice of solvent was made to simplify the analysis of the infrared spectra. Discrimination of the adsorbed molecules from those in the liquid phase was achieved by recording p/s polarization ratios to take advantage of the so-called surface selection rule,[13] and a number of tests were performed to ensure that the recorded spectra do indeed correspond to adsorbed species.[14] For one, in spectra from liquid film of increasing thickness, the peaks due to the solvent grow, while those assigned to the adsorbate do not change at all. In addition, the absorption bands persist after flushing the system with pure carbon tetrachloride, an indication of the high degree of irreversibility of the adsorption. Finally, no infrared peaks were detected on an oxidized platinum surface; the chemisorption of cinchonidine only occurs on clean metallic platinum.

Retention of the molecular structure of the cinchona modifier upon adsorption is evidenced by the permanence of the main quinoline in-plane deformation modes around 1591, 1568, and 1507 cm^{-1} (although the latter two shift to 1574 and 1510 cm^{-1}, respectively). On the other hand, it is clear that the surface induces a specific adsorption configuration. In particular, the increase in relative importance of the peak at 1462 cm^{-1} with respect to that at 1452 cm^{-1} in the chemisorbed species (the C_7 and C_5 CH_2

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10.1021/ja016722n CCC: $20.00

scissoring vibrations of the quinuclidine ring, respectively) points to a well-defined orientation of the amine ring with respect to the surface. Also, the blue shift of the peak around 1230 cm^{-1} (from 1228 cm^{-1} in the pure solid to 1236 cm^{-1} when adsorbed on the surface), which we assign to a quinoline C−H deformation mode, indicates rehybridization of those bonds due to a strong interaction with the metal, and corroborates the anchoring role of that aromatic ring on the surface.

It was found here that the initial concentration of the modifier in the carbon tetrachloride solution controls its adsorption geometry and, with that, the performance of the catalyst. In particular, three distinct adsorption regimes were identified: (1) below 5% of saturation, where no adsorbed species are detected, (2) between 5 and 20%, at which point three weak peaks are seen at 1217, 1255, and 1385 cm^{-1}, and (3) above 20%, which yields complex infrared spectra dominated by bands about 1462 and 1512 cm^{-1}. The latter concentration range can be easily associated with a molecular adsorption where the quinoline ring is tilted on the surface, because most of the vibrational signals observed in the spectra correspond to modes with dipoles in the plane of that ring.[13] The intermediate regime is a bit more difficult to assign, but most likely reflects a flat-lying geometry, given the absence of the ring-breathing modes and the fact that the three observed features are due to deformations in the quinuclidine ring. What we find particularly interesting is the excellent correlation between these different adsorption arrangements and the variations in activity and enantioselectivity of the cinchona/Pt system during the chiral hydrogenation of ketoesters.[8] This is highlighted by the data in Figure 2, which show how the maximum enantioselectivity is reached at concentrations corresponding to the flat-lying adsorption geometry of the modifier, that is, for cinchona-to-platinum atom ratios around 0.1. It can be speculated that lower concentrations are not enough to cover the surface with a sufficient number of modifier molecules to induce chirality, while higher concentrations lead to surface crowding, forcing the aromatic ring to tilt on the surface, and the catalyst to lose its enantioselective functionality.[15]

It should be pointed out that our experiments were carried out with CCl_4 as the solvent, while the enantioselectivity data in Figure 2 were obtained using acetic acid instead. The nature of the solvent is critical in the performance of these systems,[10] a fact corroborated by our own studies.[14] Nevertheless, results from additional RAIRS experiments led us to expand our conclusion that the conditions used for enantioselective catalysis affect the adsorption geometry of the chiral modifiers, and that such geometry defines the activity and enantioselectivity of the catalytic process.[14] In general, the conditions that favor a flat-lying adsorption of the aromatic ring of the modifier increase the activity and enantioselectivity of the platinum catalyst. Future in situ characterization studies such as these should allow for the systematic optimization of chiral heterogeneous catalytic processes.

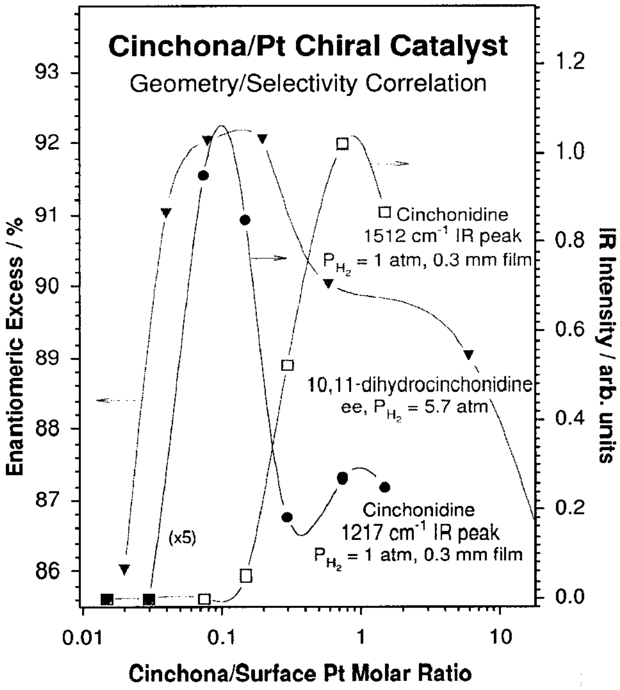

Figure 2. Signal intensities for the infrared features corresponding to flat-lying (1217 cm^{-1}, ●) and tilted (1512 cm^{-1}, □) adsorption geometries as a function of cinchonidine concentration in the carbon tetrachloride solution. These variations in adsorption geometry correlate well with reported changes in activity and enantioselectivity of a platinum catalyst modified with 10,11-dihydrocinchonidine toward the hydrogenation of ethyl pyruvate in acetic acid (▼).

Acknowledgment. Finance for this project was provided by grants from the Petroleum Research Fund of the American Chemical Society and the National Science Foundation. We also thank Dr. Yongkui Sun for helpful discussions, and Dr. Encarnacion Montecino-Rodriguez for her help in the final editing of the manuscript.

JA016722N

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