In-Situ Raman Investigation of an Enantioselective Catalyst: Cinchonidine Interactions with Polycrystalline Platinum

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Summary
The vibrational properties of adsorbed cinchonidine on polycrystalline platinum in ethanol solutions have been probed in situ using surface-enhanced Raman spectroscopy (SERS). Analysis of the SER spectra indicates that the chiral modifier is adsorbed through the quinoline portion of cinchonidine by π-bonding with the Pt surface. Consideration of surface selection rules suggests that the cinchonidine is at least somewhat tilted with respect to the platinum surface over a wide range of cinchonidine liquid-phase concentrations (at least from 50 µM to 1.2 mM). Temperature dependence of adsorption appears consistent with observed trends in the enantioselectivity of this catalytic system.

Introduction
One of the most successful approaches in the development of heterogeneous enantioselective catalysts has involved modification of supported transition-metal catalysts by adsorption of chiral molecules on their surfaces during reaction [1]. In particular, the asymmetric hydrogenation of α-ketoesters over cinchona alkaloid-modified platinum catalysts has received much attention. To explore the adsorption of the chiral modifier cinchonidine on platinum, we have been using the vibrational spectroscopic approach of surface-enhanced Raman spectroscopy (SERS).

Experimental
The polycrystalline SERS-active platinum films were prepared using a method described in the literature [2]. Raman spectra were obtained using a LabRam confocal Raman microscope (JY Horiba), which operates in the dispersive mode and utilizes a charge coupled device (CCD) detector.

Results and Discussion
Figure 1 shows typical in-situ SER spectra for platinum immersed in pure ethanol (middle spectrum) and in ethanol containing 1.2 mM cinchonidine (top spectrum) at 25ºC. Also shown for comparison is the normal Raman of solid cinchonidine. We first focus on the large SERS peak at 1355 cm⁻¹, which is assigned to a quinoline ring stretching mode of cinchonidine adsorbed on Pt. This vibrational feature is instructive in two ways. First, the width of the peak is broadened significantly from solid-phase value, increasing from ca 6 cm⁻¹ to ca 30 cm⁻¹. Second, the peak is redshifted ca 10 cm⁻¹ upon cinchonidine adsorption. Both of these observations suggest that the quinoline group of the cinchonidine is interacting strongly with the Pt surface, likely by π-bonding through the aromatic rings, as has been suggested [3-5]. Furthermore, at this relatively high concentration it appears that the cinchonidine is
tilted with respect to the surface. One piece of evidence supporting this claim is the appearance of SERS bands at 1512, 1572, and 1587 cm\(^{-1}\), corresponding to the quinoline in-plane ring deformation modes. Since these vibrations are in the plane of the aromatic rings, they would be expected to be very weak in the SER spectra if the quinoline portion of the molecule is adsorbed “flat” with respect to the surface. Thus, their presence suggests at least a slight tilt under these conditions. Further evidence for a tilt is provided by the observation of a SERS peak at ca 3089 cm\(^{-1}\) (not shown in Fig. 1), corresponding to an in-plane aromatic C-H.

SER spectra were also obtained over a wide range of cinchonidine concentrations. The trend in the SER spectra was for in-plane modes to be enhanced preferentially over out of plane modes. This observation suggests that the degree of tilt with respect to the surface is increasing as the concentration is increased. Thus, it appears that this is consistent with the current interpretation that a predominantly “flat” or only slightly tilted cinchonidine (at lower liquid-phase concentrations)) is responsible for the observed catalytic behavior. Finally, the effects of temperature were examined. It was determined that the cinchonidine begins to desorb from the platinum surface at around 50°C in the presence of hydrogen. This is consistent with observed deterioration of enantioselectivity that has been observed at temperatures greater than 50°C. The cinchonidine is simply not able to stick on the platinum surface at such elevated temperatures.

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References