Surface Raman characterization of cinchonidine-modified polycrystalline platinum in ethanol: effects of temperature and comparison with 10,11-dihydrocinchonidine

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Abstract

The adsorption of the chiral modifier cinchonidine on platinum in ethanol as a function of temperature has been studied with surface-enhanced Raman spectroscopy (SERS). The temperature range chosen was from 30 to 70 °C, within which both the activity and selectivity of cinchonidine-modified Pt catalysts have been shown to change dramatically. Platinum surfaces were modified with 260 μM cinchonidine in ethanol, and examined both in pure ethanol and in the modifying solution itself. Adsorbed cinchonidine under pure ethanol was found to partially desorb as the temperature was raised, accompanied by an increase in the average tilt of the quinoline group with respect to the surface. In contrast, the presence of solution-phase cinchonidine resulted in an increase in the cinchonidine surface coverage and average tilt as temperature was raised. In a previous study [J. Mol. Catal. A 212 (2004) 277] we showed that hydrogen causes a dramatic enhancement in the SERS response of adsorbed cinchonidine. This was attributed to a conversion of cinchonidine to 10,11-dihydrocinchonidine on the Pt surface and a more flat orientation of the quinoline group. In both pure ethanol and in 260 μM cinchonidine, the presence of hydrogen causes a significant decrease in the alkaloid SERS bands at temperatures above 40 °C. In addition, the average tilt of the quinoline group increases significantly at these elevated temperatures. The temperature-dependence of 10,11-dihydrocinchonidine adsorption was also investigated, and is almost identical to that observed for cinchonidine in the presence of hydrogen. This lends further support to the conclusion that cinchonidine is being hydrogenated on the Pt surface in the presence of hydrogen. The significant changes observed on the cinchonidine-modified Pt surface above 40 °C correlate well with reported decreases in enantioselectivity and turn-over frequency at similar temperatures during ethyl pyruvate hydrogenation.
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1. Introduction

Regulatory and economic pressures are driving research towards the development of green chemical processes. Heterogeneous catalysts have the potential to make a large impact on this area [1]. Reduction of the amount of solvent required, a decrease in the number of steps, and ease of catalyst handling and separation are among the possible advantages offered by the heterogeneous catalytic synthesis of fine chemicals, including enantio-pure intermediates. The Orito

reaction is perhaps the most successful laboratory scale heterogeneous enantioselective catalytic system that has been studied [2]. The reaction involves the use of cinchona alkaloids as modifiers of Pt catalysts, that allow for enantioselective hydrogenation of C=O containing molecules, such as ethyl pyruvate.

The kinetics of enantioselective ethyl pyruvate hydrogenation have been well investigated, and several studies have hinted at complex surface interactions [2–6]. The reaction can proceed to high enantioselectivities with only trace quantities of alkaloid present in the solution, thus demonstrating the strong affect that cinchonidine has on the hydrogenation. The enantioselectivity also changes as a function of the amount of cinchonidine with respect to the platinum surface

area, with the optimal value being around 1 cinchonidine per 10 exposed Pt atom [2]. There is also at least an order of magnitude increase in the reaction rate when compared to what is observed in the absence of modifier, which shows a strong interaction with the rate controlling steps involved in the hydrogenation. Isotopic deuterium hydrogenation and exchange studies of cinchonidine on Pt [7–9] have shown that the quinoline group of the cinchonidine is directly interacting with the surface under reaction conditions, thus leading to a very specific orientation on the surface. Ultra-high vacuum (UHV) studies [10–12] of Pt surfaces dosed with cinchonidine [10] and related molecules suggest that there is no long-range ordering within the adsorbed monolayer. Thus, the increase in enantioselectivity appears to be due to a one-on-one interaction of the adsorbed cinchonidine modifier with the reactant. Clearly, elucidating the nature of the modifier-surface interaction is a key to understanding this complex catalytic system.

In the past few years, there has been an increased effort to employ in situ spectroscopic approaches to the study of this reaction system. Reflection absorption infrared spectroscopy (RAIRS) [13–15], attenuated total reflection infrared (ATR-IR) spectroscopy [16–18], and surface-enhanced Raman spectroscopy (SERS) [19–21] have been employed to examine model Al_2O_3-supported Pt [16,17] and Pd [18], and polycrystalline Pt [13–15,19–21]. The main focus has been the effects of solvent and surface coverage on the orientation of the adsorbed cinchonidine. To date, all of these studies have been preformed at around 20–25 °C. However, it is well known that increasing the temperature has a dramatic (and usually detrimental) effect on the enantioselectivity and reaction rate [3,22–26]. Blaser et al. [3,22], Sutherland et al. [24], and Kunzle et al. [25] have studied the kinetics of the Orito reaction as a function of temperature. They found a significant drop in enantioselectivity and/or turn-over frequency (TOF) as the temperature is increased above 40 °C. For example, the results reported by Kunzle et al. [25] show a roughly constant TOF, with a sharp drop in enantioselectivity. However, the experimental conditions used were in a mass transfer limited regime. Thus, these observations were most probably the result of mass transfer limitations rather than actual surface kinetics. Evidence for desorption of the modifier under liquid-phase conditions is provided in a study by Augustine et al. [23]. Measurements of the supernatant liquid used to modify the experimental catalyst showed the remaining quantity of alkaloid left in the solution phase. As the temperature of the modification bath was increased the concentration of alkaloid remained roughly constant until above 40 °C, where there was a significant increase in concentration. This showed that the 10,11-dihydrocinchonidine used to modify the surface desorbed into the solution phase at these elevated temperatures.

In this paper, we explore the interaction of cinchonidine with a platinum surface in ethanol as a function of temperature using surface-enhanced Raman spectroscopy. The effects of solution-phase H_2 at elevated temperatures

are also studied. Finally, the temperature-dependence of 10,11-dihydrocinchonidine adsorption on Pt is probed for comparison, given that this species is proposed to be the most effective form of the modifier on the surface. We believe this to be the first surface spectroscopic study of these temperature effects under conditions relevant to the actual catalytic reaction environment.

2. Experimental

2.1. Materials

Cinchonidine (Fluka, 98%), 10,11-dihydrocinchonidine (Merck), ethanol (Aldrich, 99.5%), dihydrogen hexachloroplatinate (Premion, 99.95%), sodium phosphate (Fisher), and hydrogen (National Welders, UHP) were all used as supplied. All water used for these experiments is purified via a Barnstead B-pure initial low inorganic filtration followed by filtration with a Milipore low organic series to ca. 18 MΩ/cm resistance.

2.2. SER active platinum preparation

SERS-active Pt substrates consist of thin Pt over-layers deposited on roughened gold electrodes. Gold electrodes were prepared using gold wire (Premion, 99.99%, 1.4 mm diameter) and a Teflon rod (Dupont). The rod is bored with a concentric hole (ca. 1 mm) and a length (ca. 2 mm) of gold wire is press fit into one end. The electrical contact is formed from a stainless steel screw fit into the opposite end of the bored hole. These surfaces were then polished in stages down to a 0.05 μm alumina powder. Electrochemical treatments were then performed using an EG&G M273A potentiostat, with potentials referenced to a saturated calomel electrode (SCE). The SERS active substrate is prepared by holding the potential of the gold surface at −0.3 V in a deaerated aqueous 0.1 M KCl solution for 30 s, sweeping the voltage to 1.2 V at 500 mV/s, holding at 1.2 V for 1.1 s, and then sweeping back to −0.3 V at 500 mV/s. This cycle is repeated 25 times to achieve optimal SERS activity [27]. Platinum is plated onto SERS active gold from a deaerated-aqueous solution containing 5 mM H_2PtCl_6 and 0.7 M Na_2PO_4 by holding at a constant current of 15 μA for 90 s [27].

2.3. Instrumentation

A confocal Raman spectrometer (LabRam, JY Horiba) with a custom-built liquid flow cell is used for all measurements discussed herein. The LabRam is equipped with a liquid-nitrogen cooled charged coupled device (CCD) detector, and a HeNe (632.817 nm) laser for excitation. A robotic stage is used to move the sample in micrometer increments under the spectrometer optics, thus allowing spectra to be obtained from multiple points in a controlled fashion. The spectra reported here represent an average of

spectra acquired from at least 100 different spots on the Pt surface, using a spectral acquisition time of 1 s per spot. A stainless steel liquid flow cell, which has been designed in house, allows the Olympus microscope stage of the LabRam instrument to image the flat sample surface. The details of the entire experimental apparatus are provided in a previous publication [20]. The temperature of the surface and the liquid were controlled using a Fisher Scientific temperature controller and thermocouple, a heating cord for controlling the temperature of the flow cell and Pt surface, and a heating/stirring plate to control the temperature of the external bath.

As described previously [20], cinchonidine was found to be very difficult to remove from the flow cell between experiments. Thus, the following procedure was developed. The flow-cell was baked at 300 °C in air for 2 h, followed by washing with an acidic detergent to remove the remainder of the carbonaceous species. The cell was then rinsed with deionized water, followed by a final rinse in ethanol before introduction of a fresh SERS-active Pt surface.

2.4. Temperature-dependent experiments

Temperature-dependent experiments were all preformed using freshly prepared SER active Pt electrodes in flowing ethanol. Spectra over the entire range of 300–2300 cm^{-1} were obtained. Spectroscopic data was treated and analyzed according to methods that have been previously published [20]. Cinchonidine was added to the ethanol reservoir to achieve the desired concentration via injection of a stock solution (0.01 M cinchonidine in ethanol). For those experiments involving modified surfaces only (i.e. cinchonidine no longer present in the solution-phase), the electrodes were first modified in situ, and then the solution containing cinchonidine was flushed from the system with pure ethanol. For all the experiments presented here, we have utilized a liquid phase concentration of 260 μM cinchonidine in ethanol to modify the surface. As reported previously, this concentration produces a surface signal that is ca. 70% of the full surface saturation value that can be obtained in ethanol [20]. Spectra were acquired in the flowing solution after an equilibration time of at least 15 min at each temperature, which allowed the surface environment to reach a steady state (as judged by an unchanging spectra). The temperatures explored ranged from 20 °C to near the normal boiling point of the ethanol solvent (i.e. 78.5 °C).

3. Results and discussion

In many kinetic studies of the Orito reaction system, the experiments are carried out in one of two ways. One method involves modification of the surface in an external bath, followed by transfer into the reaction mixture. The other procedure is to add cinchonidine directly into the reaction mixture with the catalyst. The advantage of the latter method is that cinchonidine is present in solution during the reaction, and can replenish the surface if required. In the following sections, we first examine the adsorption of cinchonidine on Pt in ethanol as a function of temperature, both in the presence and absence of solution-phase cinchonidine. This is followed by the effects of solution-phase hydrogen on this behavior, a situation much closer to that encountered during enantioselective hydrogenation reactions. Finally, temperature-dependent behavior of cinchonidine in the presence of hydrogen is compared to the behavior of adsorbed 10,11-dihydrocinchonidine.

3.1. Temperature-dependent adsorption of cinchonidine

The case of cinchonidine adsorption on Pt in ethanol as a function of temperature was first considered. Since surface cinchonidine was found to be irreversibly adsorbed at room temperature [20], the SERS spectra obtained with and without cinchonidine in solution look identical. Fig. 1 shows a set of SER spectra corresponding to cinchonidine-modified Pt under pure ethanol at 30 °C (top) and 70 °C (bottom). As has been discussed previously [19–21], the SER spectra for this system are complicated by the presence of significant Raman scattering from bulk ethanol and surface carbonaceous impurities. We have therefore employed spectral curve-fitting to remove these unwanted contributions from
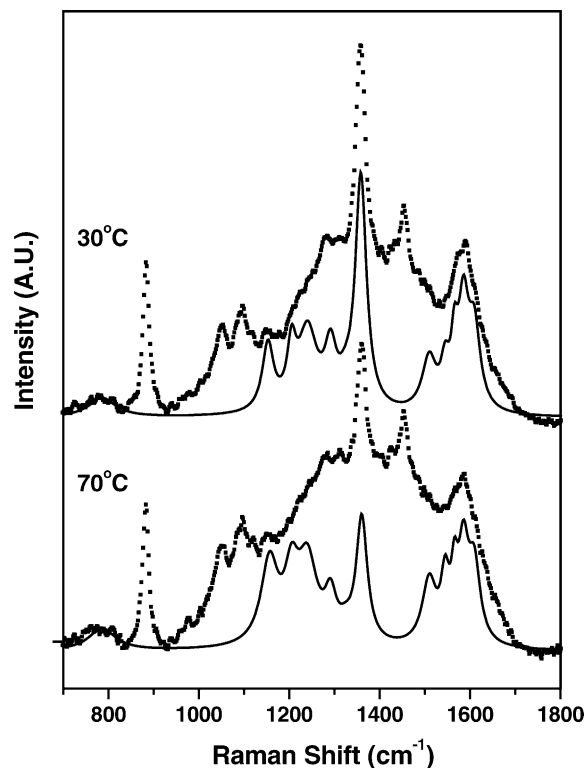

Fig. 1. SER spectra of adsorbed cinchonidine in pure ethanol at 30 °C (top) and 70 °C (bottom). The filled squares represent the raw spectral data, while the solid lines represents the SER spectra extracted from an overall fit of the raw data. See text for details.

the SER spectra. The detailed curve-fitting procedure for has been detailed elsewhere [20]. Briefly, the known peaks for liquid ethanol and surface carbon are fit, along with peaks for surface cinchonidine, for every spectrum in a series. In Fig. 1, the overall Raman spectra (filled squares) contain peaks from liquid ethanol (882, 1051, 1095, 1276, and 1456 cm^{-1}), very broad features at 1580 and 1340 cm^{-1} associated with surface carbon [28,29], and a series of peaks from adsorbed cinchonidine [20,21]. The solid lines are the composite curves of all the individual peaks for adsorbed cinchonidine.

As the temperature is changed from 30 to 70 °C, almost all of the peaks are seen to decrease. However, the ratios between the peaks change substantially. Following these changes allows for the effects of temperature on cinchonidine adsorption to be determined. The prominent band at 1357 cm^{-1} has been assigned to an aromatic ring stretching mode of cinchonidine adsorbed on Pt [21]. The specific stretching involves the carbon atoms located at the junction between the pyridine and benzene parts of the quinoline group. This peak can be used to roughly track the surface concentration of cinchonidine. To discern changes in surface molecular orientation of the quinoline group, band intensity ratios of SERS peaks are used [30–33]. For the purposes of the present investigation, we have focused on the ratio of the strong in-plane C=C stretching mode at 1587 cm^{-1} to the out-of-plane C–H wagging mode at 784 cm^{-1}. However, the other prominent in-plane C=C vibrations at 1512 and 1572 cm^{-1} show similar behavior with temperature.

Fig. 2A plots the relative intensity of the 1357 cm^{-1} band as a function of temperature from a treated surface under flowing ethanol. The intensities have been normalized to the value obtained at 30 °C. As temperature is increased to 70 °C, the signal decreases constantly across the temperature range, suggesting a decrease in the coverage of cinchonidine on the surface. This trend is irreversible, showing that the resulting small level of solution-phase cinchonidine does not re-adsorb as the temperature is reduced back to 30 °C. There are also no new peaks that can be clearly observed at elevated temperatures (cf. Fig. 1), suggesting that the cinchonidine is not reacting or dissociating on the surface at any detectable level.

We have reported previously that the ratio of the 1587 cm^{-1} in-plane vibration to the 784 cm^{-1} out-of-plane vibration of adsorbed cinchonidine at room temperature is around 4–5 when the liquid-phase cinchonidine concentration of 260 μM [20]. For the plots presented here, the ratios have been normalized to the ratio obtained at 30 °C in order to more clearly show the changing trend as a function of temperature, and to facilitate comparisons between samples under different conditions. Fig. 2B plots this relative 1587 cm^{-1}/784 cm^{-1} band intensity ratio as a function of increasing temperature. The ratio is seen to increase as the temperature is raised, suggesting an increase in the average tilt angle of the quinoline group with respect to the platinum surface.
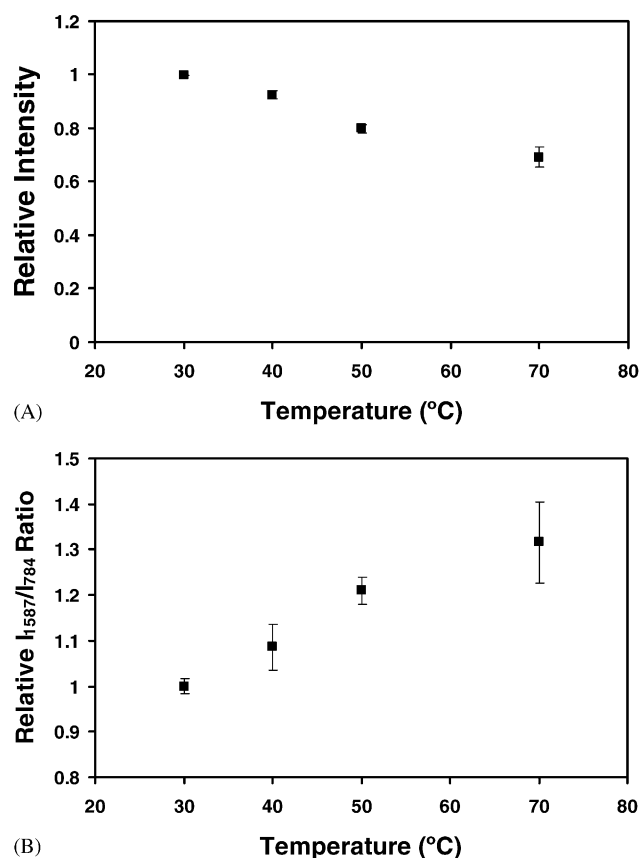

(A)

(B)

Fig. 2. SERS band intensity trends as a function of temperature for adsorbed cinchonidine on Pt in pure ethanol. (A) Relative intensity of the 1357 cm^{-1} in-plane ring stretching vibration, with the scale normalized to the intensity obtained at 30 °C. (B) Ratio of the 1587 cm^{-1} in-plane band intensity to the 784 cm^{-1} out-of-plane band intensity, with the scale normalized to the ratio obtained at 30 °C.

We next examined the case where cinchonidine was present in the solution phase at a concentration of 260 μM. Fig. 3A shows how the relative intensity of the 1357 cm^{-1} peak varies as a function of temperature under these conditions. As the temperature is increased, the signal from the surface initially increased, but then leveled off. This suggests that the cinchonidine in solution is sufficient to continually replenish the surface with cinchonidine. In contrast to the case of pure ethanol, the intensity returns (i.e. there is no hysteresis) as the temperature is decreased from 70 °C back to 30 °C. This suggests that the cinchonidine desorption is reversible and that the surface is not being blocked with fragments from dissociation at the higher temperatures. Fig. 3B shows how the orientation of the quinoline group varies with temperature under this concentration by again plotting the relative intensity ratio of the 1587 cm^{-1} band to the 784 cm^{-1} band. The tilt angle of the quinoline group is seen to increase with temperature to 40 °C and then remain constant. Such behavior is consistent with the apparent increase in surface coverage observed in Fig. 3A. As the aromatic group stands up on the surface, there is a greater interaction of the quinoline
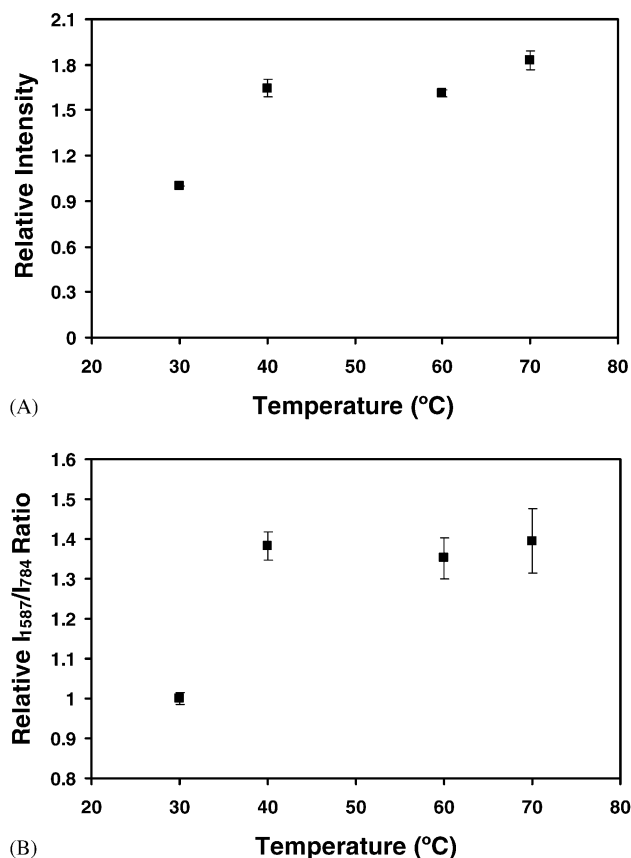
(A)

(B)

Fig. 3. SERS band intensity trends as a function of temperature for adsorbed cinchonidine on Pt in 260 μM cinchonidine in ethanol. (A) Relative intensity of the 1357 cm^{-1} in-plane ring stretching vibration, with the scale normalized to the intensity obtained at 30 °C. (B) Ratio of the 1587 cm^{-1} in-plane band intensity to the 784 cm^{-1} out-of-plane band intensity, with the scale normalized to the ratio obtained at 30 °C.

nitrogen with the surface, and more free sites for adsorption become available. However, another contributing factor to this increase may be the freeing up of some adsorption sites by removal of carbonaceous species. The bands associated with this species at 1580 and 1340 cm^{-1} are observed to decrease by around 15% (data not shown) at 40 °C and then remain constant at higher temperatures, suggesting that the coverage of this species has decreased on the surface.

3.2. Effects of H$_2$ on the temperature dependence of cinchonidine adsorption

While the above temperature-dependent adsorption behavior of cinchonidine in ethanolic solution is interesting from a fundamental standpoint, actual catalytic systems involve the interaction of cinchonidine with adsorbed hydrogen. Recent vibrational spectroscopic studies have shown that hydrogen has a significant effect on the surface spectra of adsorbed cinchonidine on platinum. Using RAIRS, Ma et al. [13] observed that the presence of H$_2$ in CCl$_4$ solution resulted in a larger coverage of cinchonidine on the surface when compared to O$_2$, N$_2$, or CO$_2$ being

present. It was proposed that this effect arose from the H$_2$ being able to clean the surface of impurities, such as CO. LeBlanc et al. [20] also observed a dramatic enhancement of surface Raman scattering of adsorbed cinchonidine species when hydrogen was present in ethanol. The spectral changes were attributed to the conversion of cinchonidine to 10,11-dihydrocinchonidine on the surface, resulting in stronger adsorption and a flatter orientation of the quinoline ring. It was therefore expected that the presence of H$_2$ would affect the temperature dependence of adsorbed cinchonidine.

Fig. 4 shows a pair of SER spectra corresponding to cinchonidine-modified Pt under pure ethanol at 30 °C (top) and 70 °C (bottom) in the presence of dissolved hydrogen. The surface was first modified by flowing 260 μM cinchonidine in ethanol through the flow cell, followed by flushing with pure ethanol and then saturation of the flowing ethanol with H$_2$. This experiment in effect mimics the very common situation where the catalyst is pre-modified and then added to the reaction mixture. Just as in the case when hydrogen is not present in solution, the SERS peaks are significantly decreased at the higher temperature.

Fig. 5A and B track, respectively, how the relative intensity of the 1357 cm^{-1} band and 1587 cm^{-1}/784 cm^{-1} band intensity ratio change as a function of temperature under these conditions. The 1357 cm^{-1} band intensity increases
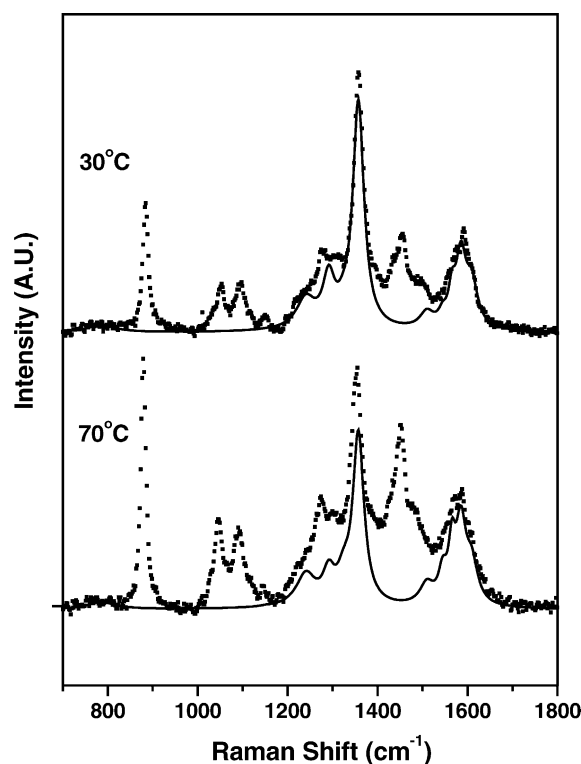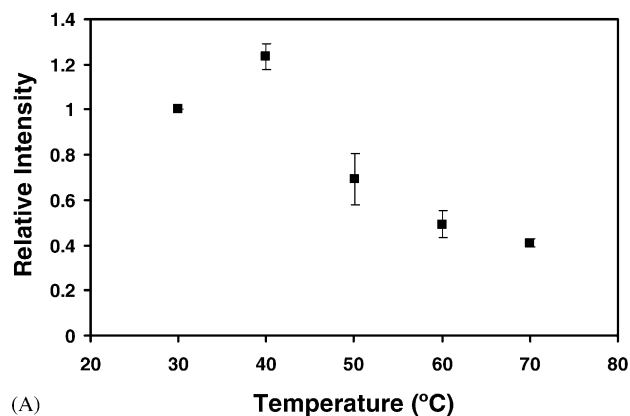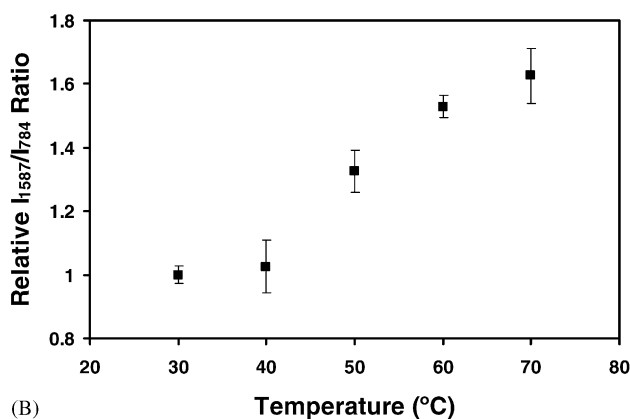

Fig. 4. SER spectra of adsorbed cinchonidine in pure ethanol saturated with H$_2$ at 30 °C (top) and 70 °C (bottom). The filled squares represent the raw spectral data, while the solid lines represents the SER spectra extracted from an overall fit of the raw data. See text for details.
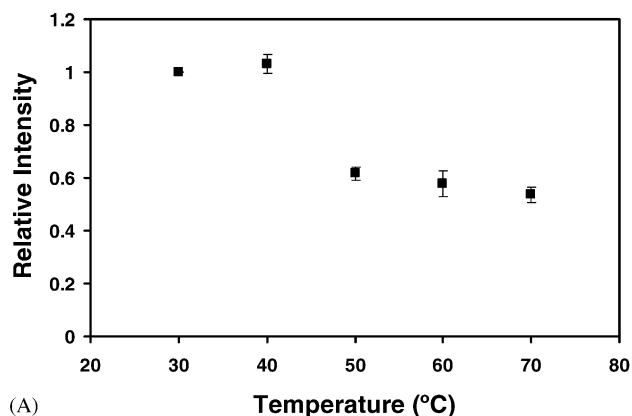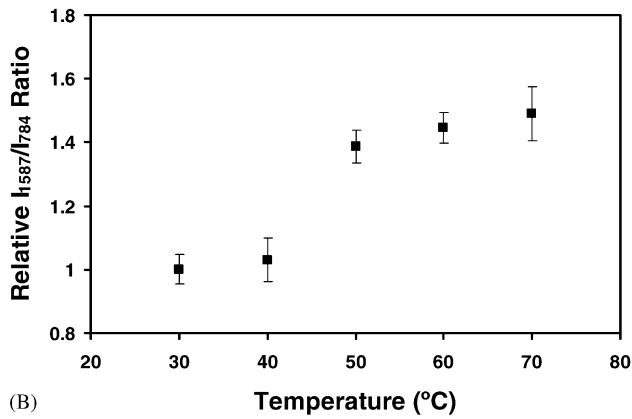
Fig. 5. SERS band intensity trends as a function of temperature for adsorbed cinchonidine on Pt in pure ethanol saturated with H_2. (A) Relative intensity of the $1357\,cm^{-1}$ in-plane ring stretching vibration, with the scale normalized to the intensity obtained at $30\,°C$. (B) Ratio of the $1587\,cm^{-1}$ in-plane band intensity to the $784\,cm^{-1}$ out-of-plane band intensity, with the scale normalized to the ratio obtained at $30\,°C$.

Fig. 6. SERS band intensity trends as a function of temperature for adsorbed cinchonidine on Pt in $260\,\mu M$ cinchonidine in ethanol saturated with H_2. (A) Relative intensity of the $1357\,cm^{-1}$ in-plane ring stretching vibration, with the scale normalized to the intensity obtained at $30\,°C$. (B) Ratio of the $1587\,cm^{-1}$ in-plane band intensity to the $784\,cm^{-1}$ out-of-plane band intensity, with the scale normalized to the ratio obtained at $30\,°C$.

by about 25% as the temperature is raised to $40\,°C$. This is accompanied by a ca. 15% decrease in the intensity of the bands associated with the surface carbonaceous impurities (data not shown). Therefore, the relatively small increase in alkaloid coverage may be accounted for by adsorption of cinchonidine onto sites that are exposed by the removal of some carbonaceous species. Such residual solution-phase cinchonidine in the desired pure ethanol is not unexpected given the affinity of this species for all the surfaces in our flow system. Upon further heating to $50\,°C$ there is a 50% loss of intensity, which continues at higher temperatures. As for the case without hydrogen in solution (Fig. 2) the intensity does not return to its original value as the temperature is decreased back to $30\,°C$. Fig. 5B shows that the average tilt of the quinoline group stays relatively constant up to $40\,°C$. However, the ratio increases by 30% at $50\,°C$, and continues to increase linearly up to $70\,°C$. Therefore, the cinchonidine that is left on the surface at $70\,°C$ has a significantly higher tilt angle than the average tilt angle at $30\,°C$. As with the surface coverage, the average tilt does not flatten back out as the temperature is returned to $30\,°C$.

The presence of cinchonidine in the liquid phase along with hydrogen has some effect on this behavior. Fig. 6A and B shows the changes in the intensity of the $1357\,cm^{-1}$ band and $1587\,cm^{-1}/784\,cm^{-1}$ band intensity ratio, respectively, when both cinchonidine ($260\,\mu M$) and hydrogen are present in the solution phase. The $1357\,cm^{-1}$ intensity increases slightly at $40\,°C$, accompanied by a ca. 15% decrease in the intensity of surface carbonaceous peaks. The $1357\,cm^{-1}$ intensity then exhibits the characteristic large drop off at $50\,°C$ and higher. However, the slope of the intensity decrease between 50 and $70\,°C$ is less than half of what was observed in Fig. 5A. This result can be understood in terms of cinchonidine being available in solution to maintain a higher equilibrium coverage. Fig. 6B shows a similar trend to Fig. 5B, in that the tilt of the quinoline group remains largely constant up to $40\,°C$, but dramatically increases with higher temperature. As the temperature is reduced back to $30\,°C$, both quantities return to their original values without hysteresis. This is due to the solution-phase material that is available for re-adsorption on the platinum, and suggests that the surface can be regenerated under these conditions.

The significant changes observed on the modified Pt surface at elevated temperature in the presence of hydrogen correlate well with reported kinetic studies of ethyl pyruvate hydrogenation [3,22–26]. Such studies show a decrease in both enantioselectivity and turn-over frequency at temperatures above 40 °C. It is therefore likely that this reduced catalytic effectiveness is caused by a combination of two effects. The first is that there is a decreased amount of modifier on the surface, which would decrease the one-on-one interaction of the adsorbed cinchonidine modifier with the reactant. Such an interaction is central to the proposed mechanism in which the reactant (e.g. ethyl pyruvate) forms a hydrogen bond with the quinuclidine nitrogen on the adsorbed cinchonidine. The second effect is that the aromatic group is much more tilted with respect to the Pt surface, which likely also results in decreased interactions between the quinuclidine nitrogen and the reactant.

3.3. Temperature dependence of 10,11-dihydrocinchonidine adsorption

There is kinetic [6,34], spectroscopic [20], and deuterium exchange [9] experimental evidence that cinchonidine is quickly converted to 10,11-dihydrocinchonidine under reaction conditions. In addition, 10,11-dihydrocinchonidine can be further converted to deeper hydrogenation products that have inferior modifying capabilities [6]. Deuterium exchange experiments have clearly shown that the first step in cinchonidine hydrogenation on Pt is hydrogenation of the vinyl group. Our recent spectroscopic studies [20] showed that the SERS spectrum for adsorbed 10,11-dihydrocinchonidine was almost identical to that obtained for cinchonidine in the presence of hydrogen at room temperature. We therefore were interested in exploring any similarities between the thermal behaviors of these two cases.

The temperature dependence of adsorbed 10,11-dihydrocinchonidine was investigated using the same liquid-phase concentration of 260 μM used for cinchonidine above. Fig. 7A follows the progression of the 1357 cm^{-1} relative band intensity as the system is heated from 30 to 70 °C. The behavior is very similar to Figs. 5A and 6A, in that there is a dramatic decrease in intensity at 50 °C which continues to higher temperatures. Likewise, Fig. 7B is similar to Figs. 5B and 6B, with the 1587 cm^{-1}/784 cm^{-1} band intensity ratio increasing at 50 °C. The increase in the tilt angle at this temperature is consistent with a previous NEXAFS study of 10,11-dihydrocinchonidine adsorption on Pt(1 1 1) in UHV [12]. While a predominantly flat orientation was found at 25 °C, the average molecular tilt was observed to increase to $60 \pm 10°$ as the temperature was raised to 50 °C. The present experiments also show the same reversibility as observed for cinchonidine with H$_2$. A major difference in the experiment presented in Fig. 7, however, is that hydrogen is not present with 10,11-dihydrocinchonidine. The observed behavior thus supports the theory that cinchonidine is actively being converted on the platinum surface
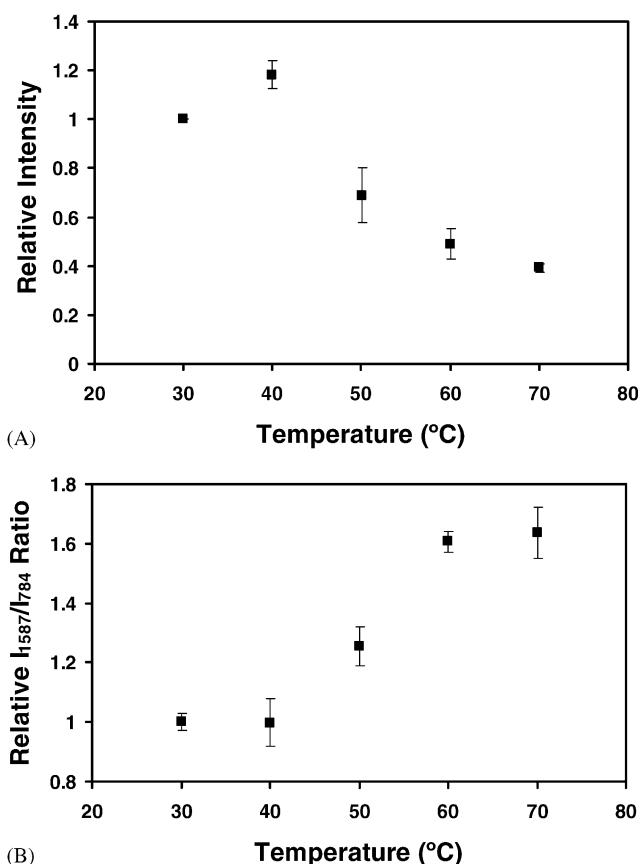

Fig. 7. SERS band intensity trends as a function of temperature for adsorbed 10,11-dihydrocinchonidine on Pt in 260 μM 10,11-dihydrocinchonidine in ethanol saturated with H$_2$. (A) Relative intensity of the 1357 cm^{-1} in-plane ring stretching vibration, with the scale normalized to the intensity obtained at 30 °C. (B) Ratio of the 1587 cm^{-1} in-plane band intensity to the 784 cm^{-1} out-of-plane band intensity, with the scale normalized to the ratio obtained at 30 °C.

to 10,11-dihydrocinchonidine when hydrogen is present in solution.

It is also interesting to compare the results obtained for cinchonidine without hydrogen (cf. Fig. 3) to the those obtained for 10,11-dihydrocinchonidine. These very similar molecules exhibit significantly different temperature-dependent surface coverage trends for the same liquid-phase concentrations. While cinchonidine surface coverage appears remains stable above 40 °C (Fig. 3), dihydrocinchonidine coverage drops by at least 50% at these temperatures. A likely explanation for this difference is the presence of the vinyl group on cinchonidine that can itself form an additional bond with the Pt surface. A strong interaction of the vinyl group with the Pt surface is implied by kinetic studies of cinchonidine hydrogenation that show that this group is the first to be hydrogenated [34]. In contrast, 10,11-dihydrocinchonidine has no vinyl group to coordinate to Pt, and thus may have a weaker interaction with the surface, at least at higher temperatures. Unfortunately, we have been unable to detect any SERS bands that are clearly associated with an adsorbed vinyl group for cin-

chonidine. The frequency of the adsorbed vibration would be expected to be within $1600–1650\,cm^{-1}$ [35], right in the range for several strong cinchonidine peaks (cf. Figs. 1 and 4). Unfortunately our signal to noise ratio is not large enough to be able to further deconvolute the spectra in this region with any degree of certainty.

4. Concluding remarks

Surface-enhanced Raman spectroscopy has been used to probe the adsorption of the chiral modifier cinchonidine on platinum in ethanol as a function of temperature. We believe that this is the first in situ surface spectroscopic study of temperature effects in this system. Platinum surfaces were modified with $260\,\mu M$ cinchonidine in ethanol, and examined both in pure ethanol and in the modifying solution itself. These conditions mimic the two types of modification protocols used extensively in enantioselective hydrogenation studies that employ this type of catalyst. Analysis of the SER spectra allowed for determination of both changes in surface coverage as well as orientation of the quinoline group to be determined in a qualitative fashion. Adsorbed cinchonidine under pure ethanol was found to partially desorb as the temperature was raised, accompanied by an increase in the average tilt of the quinoline group. In contrast, the presence of solution-phase cinchonidine resulted in an increase in the cinchonidine surface coverage and average tilt as temperature was raised. In both pure ethanol and in $260\,\mu M$ cinchonidine, the presence of hydrogen causes a significant intensity decrease in the alkaloid SERS bands at temperatures above $40\,^{\circ}C$. In addition, the average tilt of the quinoline group increases significantly at these elevated temperatures. The temperature-dependence of 10,11-dihydrocinchonidine adsorption is almost identical to that observed for cinchonidine in the presence of hydrogen. This result lends further support to the conclusion that cinchonidine undergoes hydrogenation on the Pt surface to 10,11-dihydrocinchonidine. Overall, the significant changes observed on the modified Pt surface at elevated temperature in the presence of hydrogen correlate well with reported kinetic studies of ethyl pyruvate hydrogenation. Such studies show a decrease in both enantioselectivity and turn-over frequency at temperatures above $40\,^{\circ}C$. It is therefore likely that this reduced catalytic effectiveness is caused by a combination of decreased surface coverage due to desorption and increased tilting of the remaining adsorbed cinchonidine.

Acknowledgements

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