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Surface Chemistry

Adsorption of 1-(1-Naphthyl)ethylamine from Solution onto Platinum Surfaces: Implications for the Chiral Modification of Heterogeneous Catalysts**

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Since Orito et al. reported that the hydrogenation of prochiral molecules using transition-metal heterogeneous catalysts may be made enantioselective by adding a small amount of a chiral modifier to the liquid reaction mixture,[1] there has been a great deal of interest in understanding how this chiral modification works and in extending it to other systems.[2–6] Unfortunately, it has been difficult to identify other types of chiral modifiers beyond the cinchona alkaloids and related molecules used in the initial studies. A better knowledge of the molecular mechanism that accounts for these reactions may be needed to expand the library of viable chiral modifiers. This has also become a prototypical system for the investigation of possible chiral modification of heterogeneous catalysts in general.[3,6–8]

From the fundamental point of view, much molecular-level characterization has been carried out by using 1-(1-naphthyl)ethylamine (NEA), a simpler molecule that also contains the main functionalities believed responsible for the modifying behavior of the cinchona alkaloids, namely, an aromatic ring and an amine group near a chiral center.[9–12] Although less efficiently than cinchona alkaloids, NEA has also been shown to act as a chiral modifier for the hydrogenation of some α-ketoesters.[5,13,14] The working hypothesis that has emerged is that these chiral modifiers may weakly bind the reactant at the nitrogen atom of the amine group (and perhaps also at a second molecular location, possibly via hydrogen bonding), forming a complex that may adsorb on the surface of the metal phase of the catalysts through the aromatic ring. In this "docking" model, the chirality around the binding site is alleged to provide the chiral environment for the promotion of the hydrogenation of prochiral reactants enantioselectively.

Adsorption of the modifier through an interaction of the aromatic ring with the surface of the metal has been supported by both surface-science studies under ultrahigh vacuum (UHV) conditions[15–17] and DFT calculations.[18] However, catalytic hydrogenation reactions to produce chiral compounds are typically carried out in liquid phase, and previous work has shown that the solvent can significantly affect the adsorption characteristics of the chiral modifiers.[19,20] Here we provide results from studies on the uptake of NEA and similar compounds from CCl_4 solutions onto a polycrystalline platinum surface, obtained by using in situ reflection–absorption infrared spectroscopy (RAIRS), that suggest that the adsorption of those compounds under realistic conditions is not via the aromatic ring, as stated before, but rather by involving the amine moiety.

The key information supporting our assertion comes from a comparative study of the extent of the uptake of a family of closely related compounds on the Pt surface. Specifically, the adsorption of (*S*)-(−)-NEA was contrasted to that of 1-naphthylmethylamine (NMA), with its reduced steric hindrance around the aminic nitrogen atom, (*S*)-(−)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine (s-DNE), where the hydrogen atoms in the primary amine group of NEA are substituted by methyl moieties (making it a tertiary amine and increasing the steric hindrance around the N atom), 1-ethylnaphthalene (EtN), where the amine group is absent all together, and quinoline (Q), to test the effect of the presence of a nitrogen atom in the aromatic ring as is the case in cinchona alkaloids. The corresponding RAIRS traces are reported in Figure 1.

It is clear from Figure 1 that the only molecules that adsorb to significant saturation coverages are s-NEA and NMA. The other three compounds tested (s-DNE, EtN, and Q) yield much weaker IR absorption signals for the adsorbed species (notice the 50-fold amplification factor used to display those traces). A comparison between the data for NEA versus EtN indicates that the presence of the amine group is crucial for adsorption. Further contrasting with the spectrum for s-DNE shows that the primary nature of the amine group in NEA is also important, either because adsorption involves one or more N−H bond scission steps, or because the added methyl groups crowd the region around the nitrogen atom and hampers its ability to access the metal atoms on the surface. The data provided here are not sufficient to definitively distinguish between these two possibilities. The peaks for the N−H stretching modes in NEA and NMA could in principle be used to settle this issue, but, although the original peaks seen for those compounds in solution at approximately 3300 and 3380 cm^{-1} are not present in the spectra of the adsorbed species, new shoulders are observed at lower frequencies, at around 3120–3140 cm^{-1}, which could be interpreted as due to hydrogen-bonded N−H species. Finally, the extensive uptake seen with NMA leads to the conclusion that neither the extra methyl group bonded to the carbon next to the aromatic ring nor the chirality of that atom are

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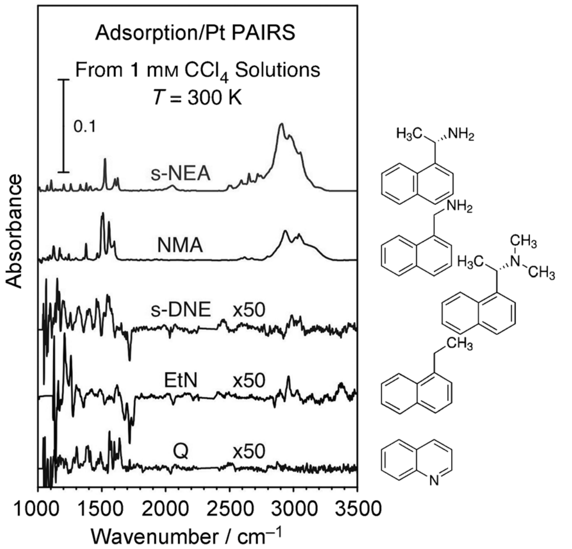

Figure 1. Reflection–absorption infrared spectra (RAIRS) for, from top to bottom, (*S*)-(−)-1-(1-naphthyl)ethylamine (s-NEA), 1-naphthylmethylamine (NMA), (*S*)-(−)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine (s-DNE), 1-ethylnaphthalene (EtN), and quinoline (Q) adsorbed from 1 mM carbon tetrachloride solutions onto the surface of a polished platinum foil. Significant uptake was observed only for s-NEA and NMA.

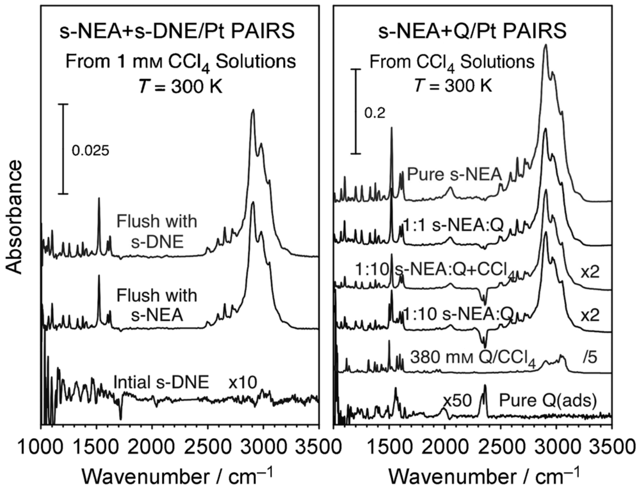

Figure 2. Left: RAIRS from displacement experiments with s-DNE and s-NEA. The Pt surface was sequentially exposed to 1 mM solutions of (from bottom to top) s-DNE, s-NEA, and s-DNE again. Clearly, NEA can adsorb on surfaces pre-exposed to DNE, whereas the opposite is not possible. Right: RAIRS for the adsorption of s-NEA and Q from mixed solutions. The spectra correspond to adsorption from 1 mM s-NEA (top trace), 1 mM s-NEA + 1 mM Q (second from top), 1 mM s-NEA + 10 mM Q (as is, fourth trace from bottom, and after flushing twice with pure CCl_4, third from top), and 1 mM Q (bottom). A transmission IR trace for a 380 mM solution of Q in CCl_4 is also provided for reference, to show that the extra features in the third trace from the top are due to Q in solution, not adsorbed on Pt. In all these cases, NEA adsorption on the Pt surface is not hindered by the presence of Q in solution.

important factors in determining the extent of adsorption. Indeed, significant uptake was also seen with (*R*)- and racemic NEA, and equally low uptake was observed with r-DNE (compared to that with s-DNE, data not shown).

A couple of alternative explanations could be summoned to explain the vastly different intensities in the IR absorption peaks seen for the various compounds in Figure 1. One possibility is that the adsorption equilibrium may be affected by the solubility of the molecules in the liquid phase. This effect was certainly proven important in determining the relative uptakes of different cinchona alkaloids.[4,19,21–23] However, in the present case, all compounds studied are liquid and fully soluble in the solvent (CCl_4).

A second explanation may be that differences in adsorption geometry may lead to different intensities of the main IR absorption peaks. In RAIRS on metals, only the perpendicular component of the dynamic dipole of a given vibration contributes to its intensity in the spectra.[24,25] In the case of cinchonidine, changes in the adsorption geometry were detected versus the concentration in solution by using this property.[26,27] It could be argued that in the cases of DNE, EtN, and Q, the molecules adsorb with the aromatic ring flat on the surface, making the in-plane ring deformation modes, which are the most intense in all these spectra (especially those between 1450 and 1650 cm^{-1}),[10,27] invisible to RAIRS. By contrast, the naphthyl rings in NEA and NMA clearly adopt a more tilted geometry, affording its detection in RAIRS.

This possibility was tested indirectly by probing the adsorption of NEA either on surfaces predosed with another molecule or in mixed solutions, in the presence of a second potential adsorbate. Representative results are provided in Figure 2. The data on the left show that sequential dosing of the Pt surface with 1 mM solutions of s-DNE, s-NEA, and back to s-DNE leads to a full NEA uptake on the DNE pre-exposed surface and to the subsequent survival of this newly formed layer upon flushing with the DNE solution. In the case on the right, it is seen that exposure of Pt to mixed solutions of s-NEA and Q always leads to the full uptake of the s-NEA, even in the presence of a ten-fold excess of Q. Similar results were obtained with other combinations. It appears that there are no "invisible" species on the surface upon exposure to s-DNE, EtN, or Q that hinder the uptake of NEA or NMA.

Similar coadsorption experiments with s-NEA and NMA show that they display similar adsorption energetics, with NMA being slightly favored. This is illustrated by the data in Figure 3. The traces in the left panel indicate that while adsorbed s-NEA can be displaced from the surface by NMA molecules from solution, the reverse is not feasible. However, the spectra in the right panel prove that this preference is marginal, and that s-NEA can be made to coadsorb with NMA if they are both deposited from a mixed solution with a slight excess of s-NEA, that is, with s-NEA:NMA ratios between approximately 1:1 and 1:0.5. It appears that the extra methyl moiety in s-NEA exerts only a minor effect on the adsorption energetics of these naphthylamines.

The main conclusion from our studies is that chiral modifiers such as NEA appear to bond to the surface of metals through their aminic nitrogen and not through interaction with their aromatic ring as commonly believed. π bonding of aromatic rings to metal surfaces is known to occur, but does not seems to dominate when the adsorption is

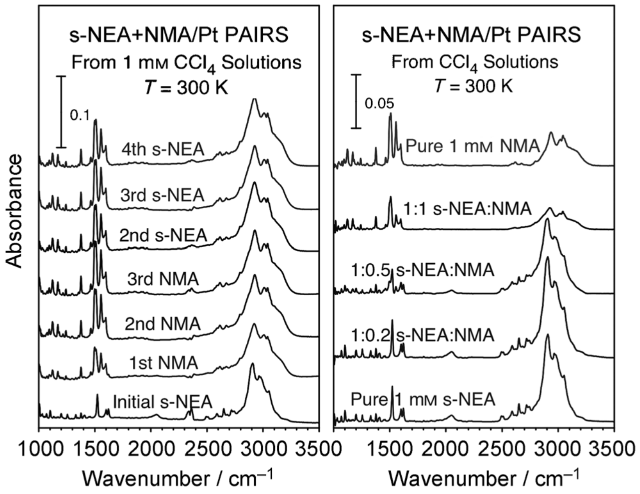

Figure 3. RAIRS from adsorption experiments with s-NEA and NMA. Left: Data from sequential exposures of the Pt surface to 1 mM solutions of (from bottom to top) s-NEA (once), NMA (three times), and back to s-NEA (four times, only 2nd, 3rd, and 4th cycles shown). NMA displaces s-NEA from the surface, and remains adsorbed upon subsequent exposures to s-NEA solutions. Right: Spectra from experiments using s-NEA + NMA mixed solutions of different compositions, as indicated in the figure. Coadsorption is possible with solutions slightly enriched in s-NEA.

from a solution. The new proposed adsorption binding may prompt a rethinking of the mechanism by which NEA and related compounds bestow enantioselectivity to metal-based heterogeneous catalysts. The formation of metal–nitrogen bonds may certainly diminish the ability of those compounds to also bind the reactant (which would likely need to happen at the same nitrogen atom), although that would in principle still be possible if adsorption takes place through the elimination of one or more aminic hydrogen atoms. It is also possible that NEA is not a good model to represent the chiral modification exerted by cinchona alkaloids. It is typically assumed that NEA, like the cinchona alkaloids, forms a one-to-one complex with the reactant to force it into a specific adsorption geometry on the surface of the metal.[11] However, there is also evidence to suggest that NEA may form supramolecular surface ensembles with chiral pockets available for the adsorption of prochiral reactants.[10,28] That mechanism is consistent with the amine-dominated adsorption mode established in the present study. Alternatively, the adsorption mode of NEA may change as a function of its concentration in solution because of changes in its equilibrium surface coverage. An analogous change in the quinoline ring orientation with concentration has been observed with cinchonidine, and correlated with its ability to bestow enantioselectivity to catalytic hydrogenation reactions.[26,29] If so, the lesson from this work may be that the changes in the adsorption geometry seen with the cinchona alkaloids may reflect not only a change in the aromatic ring orientation but also a change in the adsorption mode, from a π interaction involving the aromatic ring at low coverages to the formation of a covalent bond between the metal and the alcoholic oxygen of the cinchona at high coverages. It would be useful to extend existing quantum mechanic calculations on the adsorption of these chiral modifiers[17,30,31] to consider the new proposed adsorption mode and also to add the effect of the solvent.

Experimental Section

All the compounds used here, namely, s-NEA (> 99% purity), NMA (97% purity), s-DNE (97% purity), EtN (> 99% purity), Q (> 97% purity), and CCl_4 (99.9% purity) were purchased from Sigma–Aldrich and used as supplied. The RAIRS experiments were performed by using a cell especially designed for in situ adsorption studies from solution, described in detail elsewhere.[32] Briefly, a thin liquid film of the solution of interest is trapped between an approximately 10 mm in diameter, 1 mm thick polished polycrystalline Pt disk, which is mounted on a movable supporting rod, and a transparent trapezoidal CaF_2 prism. The IR beam from a Fourier-transform infrared spectrometer is guided through a linear polarizer and focused through the prism onto the Pt disk, and the reflected light is collected and refocused into a mercury–cadmium–telluride (MCT) detector. Spectra are acquired with both p- and s-polarized light to discriminate between adsorbed species (which show up only in the p-polarized data) and molecules in solution (visible in both p- and s-polarized spectra): the data reported here were calculated by subtracting the (appropriately scaled) s-polarized traces from the p spectra obtained with the solution of interest against the equivalent p–s background data obtained with pure CCl_4 solvent. All the reported spectra correspond to averages from 256 scans, taken with 4 cm^{-1} resolution. The Pt disk was cleaned in situ before each experiment by electrochemical oxidation–reduction cycles in 0.1 M $KClO_4$ for 1 h.

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