

## Regio-, Stereo-, and Enantioselectivity in Hydrocarbon Conversion on Metal Surfaces

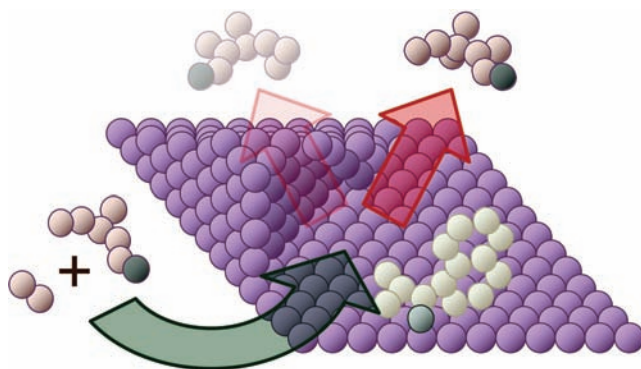
FRANCISCO ZAERA\*

Department of Chemistry, University of California, Riverside, California 92521

RECEIVED ON FEBRUARY 9, 2009

### CON SPECTUS

Selectivity is one of the most important criteria for the design of new catalytic processes. More selective catalysis could be both cheaper and greener because it does not waste reactants, does not require expensive separation procedures, and generates fewer toxic byproducts. Traditionally, control of selectivity in heterogeneous catalysis has been hampered by both a lack of understanding of the molecular details that define such selectivity and the limited range of synthetic tools available to make catalysts with the specific properties required. However, progress in surface science as well as in nanotechnology and self-assembly are providing greater molecular understanding and a wider synthetic range to address these limitations.



In this Account, we describe our studies using model systems to pinpoint the mechanistic factors that define selectivity in a number of increasingly subtle hydrocarbon dehydrogenation and hydrogenation reactions. The first examples show how the electronic properties of a metal surface affect the regioselectivity of hydrogen elimination from alkyl species adsorbed on that surface. Nickel preferentially promotes the extraction of hydrogen atoms from the carbon directly bonded to the surface, a step that leads to undesirable cracking reactions, whereas platinum allows for dehydrogenation farther down the hydrocarbon chain, facilitating a more desirable isomerization processes.

In a second set of examples, we address the issue of selectivity in alkene isomerizations involving either double-bond migrations or *cis*–*trans* interconversions. In those reactions, the key mechanistic steps require hydrogen abstraction from a  $\beta$ -carbon of the hydrocarbon chain (the second when counting away from the surface), and selectivity is defined by steric considerations around the different hydrogens available at those positions. We observed that close-packed surfaces of platinum have the unique ability to promote the thermodynamically unfavorable but highly desirable conversion of *trans*-alkenes to their *cis* counterparts, and we prepared new shape-controlled catalysts to take advantage of that valuable behavior.

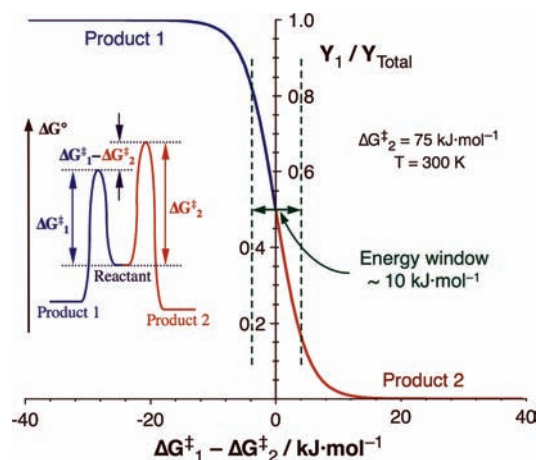
Finally, we discuss the more subtle issue of enantioselectivity. Hydrogenation of prochiral reactants such as asymmetric ketones can produce chiral compounds, but regular metal catalysts are achiral and therefore yield racemic mixtures. Fortunately, the adsorption of chiral modifiers onto a catalytic surface can bestow chirality on it. With cinchona alkaloids, individual molecules can provide the required chiral environment on the surface for such enantioselectivity. Simpler molecules may also bestow chirality on surfaces, even if that may require their assembly into chiral supramolecular structures held together by the surface. In both cases, a specific surface chiral site is produced with the help of molecular adsorbates.

The examples discussed in this Account highlight the need to design and prepare heterogeneous catalysts with sophisticated surface sites in order to promote reactions selectively. Perhaps more importantly, they also hint at some of the tools available to accomplish that task.

## 1. Introduction

In chemistry, catalysis is usually associated with the promotion of reactions so that they occur at faster rates. From a kinetic point of view, this is accomplished by opening up a new mechanistic avenue with an overall lower activation barrier. In the case of heterogeneous solid catalysts, the new chemical route involves adsorption of the reactants onto the surface, conversion of the chemisorbed species, and desorption of the products.<sup>1</sup> The search for better heterogeneous catalysts has traditionally focused on identifying the step in the new mechanism that limits the overall rate of reaction and on lowering its activation barrier to increase the overall activity. However, as catalytic processes have become more complex and as the expense of feedstocks and the polluting effects of undesirable byproducts have become more prominent factors in the design of industrial processes, the issue of selectivity has come to the forefront. For selectivity what is important is not the absolute height of the activation barrier of the rate-limiting step but rather the relative heights of the barriers of the several competing pathways available to the adsorbed species (Figure 1).<sup>2</sup> This is a more subtle problem that may in fact require dealing with the relative kinetics of fast reactions.

Over the past decade or so, the research in our group has addressed the issue of selectivity in catalysis from a molecular-level perspective.<sup>2,3</sup> Our focus has been mainly on the conversion of hydrocarbons on transition metal surfaces.<sup>4,5</sup> Mechanistic studies using model systems, often single-crystal surfaces under well-controlled ultrahigh vacuum (UHV) environments, have been carried out to characterize the kinetics of surface elementary steps involving key hydrocarbon intermediates. The knowledge developed from that work has then been extrapolated to and tested in more realistic systems, under conditions closer to those used in practical applications. What we have learned is that, indeed, controlling selectivity in hydrocarbon conversions can be quite difficult, because in many instances it involves competition among very similar hydrogenation or dehydrogenation steps with only marginally different activation energies. In fact, the more similar the competing products are in a particular process, the harder it is to design a selective heterogeneous catalytic system for it. On the other hand, we have shown that this is still possible, by, for instance, tuning the electronic properties of the solid used as catalyst or the structure of its surface. In this Account, we briefly summarize some key conclusions from our studies on a few selected cases of increasing subtlety.

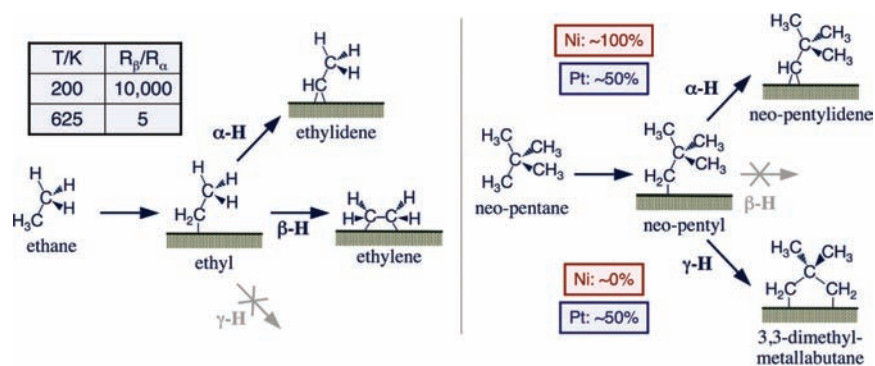


**FIGURE 1.** Energetics of Selectivity. (Inset) Depiction of a one-dimensional potential energy surface for the competitive conversion of a reactant into two possible products. The diagram highlights the fact that while reaction rates are determined by their absolute activation barriers,  $\Delta G_1^\ddagger$  and  $\Delta G_2^\ddagger$ , reaction selectivity is controlled by the difference between two. (Main) Calculated selectivity for this two-reaction system as a function of  $\Delta G_1^\ddagger - \Delta G_2^\ddagger$ . A relative variation of only  $\sim 10\%$  in absolute barrier heights can lead to an almost complete switch in selectivity from one product to the other.

## 2. Regioselectivity in Alkyl Dehydrogenation

Several of the examples reported below involve the surface chemistry of adsorbed alkyl species. Alkyl moieties are often formed upon activation of alkanes, a step central to many hydrocarbon-conversion catalytic reactions such as oil refining, natural gas conversion, food processing, and fine chemical synthesis.<sup>6</sup> However, since alkane activation is often the rate-limiting step in those processes, the isolation and characterization of the resulting alkyl intermediates is difficult to accomplish. It has also been a challenge to identify the individual steps that such alkyls follow on surfaces and to understand the factors that control selectivity during their further conversion. Fortunately, our early development of the use of alkyl halides as precursors for the preparation of alkyl groups cleanly on surfaces<sup>7</sup> has allowed us and others to investigate this surface chemistry in detail.

The main lesson that has derived from those studies is that the dehydrogenation of adsorbed alkyl moieties can take place at different positions within their molecular structure, at the  $\alpha$ ,  $\beta$ , or  $\gamma$  carbons of the hydrocarbon chain (as they are labeled in order of distance away from the surface), and that removal of a hydrogen atom from each of those positions leads to different products.<sup>5,8,9</sup> Our early work indicated that, by far, the faster dehydrogenation step involving alkyl adsorbates is from the  $\beta$  position,<sup>10</sup> the same as in organometallic chemistry.<sup>8</sup> This step leads to the formation of alkenes and to



**FIGURE 2.** Two mechanistic examples of regioselectivity in hydrocarbon dehydrogenation reactions on metal surfaces. Left, comparison between  $\alpha$ -H and  $\beta$ -H elimination from ethyl groups bonded to Pt(111) surfaces. In general, the latter is faster than the former, but because elimination from the  $\alpha$  position displays a higher activation energy, the difference becomes smaller at the temperatures typically used in hydrocarbon reforming. Right, contrast between  $\alpha$ -H and  $\gamma$ -H elimination steps. The former clearly dominates on nickel substrates, whereas the rates of both are comparable on platinum surfaces.

fast alkane–alkene equilibria in catalysis.<sup>11</sup> However, dehydrogenation steps at other positions, albeit slower, are required to promote most other catalytic reactions.

Rates for  $\alpha$ -H elimination have been measured directly from methyl moieties<sup>12–14</sup> but have also been estimated relative to  $\beta$ -H elimination from ethyl species.<sup>15,16</sup> On platinum, as on most metals, elimination from the  $\beta$  position can be several orders of magnitude faster, but the difference is less at higher temperatures: at 625 K, a temperature within the range of those used in many catalytic processes, the rates for  $\alpha$ -H and  $\beta$ -H eliminations differ by only a factor of 5 (Figure 2, left).<sup>5</sup> Additional comparisons between  $\alpha$ -H and  $\gamma$ -H eliminations using neopentyl intermediates indicated that on nickel  $\alpha$ -H elimination, a step believed to lead to undesirable C–C bond-breaking and hydrogenolysis reactions, dominates,<sup>16,17</sup> whereas on platinum the rates of both steps are comparable (Figure 2, right).<sup>18,19</sup> This is likely to be the reason why platinum is a particularly good catalyst for reforming catalysis.

The general picture that emerges is one where the nature of the catalyst plays a central role in determining selectivity. Most transition metals are good dehydrogenation catalysts but promote  $\alpha$ -,  $\beta$ -, and  $\gamma$ -H eliminations with different relative efficiencies, and that is what really matters in terms of selectivity.<sup>5</sup> For instance, nickel is a particularly good promoter of undesirable  $\alpha$ -H elimination steps, whereas platinum is comparatively efficient at promoting the  $\gamma$ -H elimination steps that lead to desirable alkane isomerizations. It may in fact be possible to use the correlation identified between this selectivity and the %d character of the metal<sup>20</sup> to fine-tune dehydrogenation catalysis via alloying. The structure of the surface may also contribute to define the relative rates of these dehydrogenation steps,<sup>4,14,20,21</sup> but if so, that is a less marked effect.

A subtler example of regioselectivity is seen in the case of the migration of carbon–carbon double bonds in alkenes. The

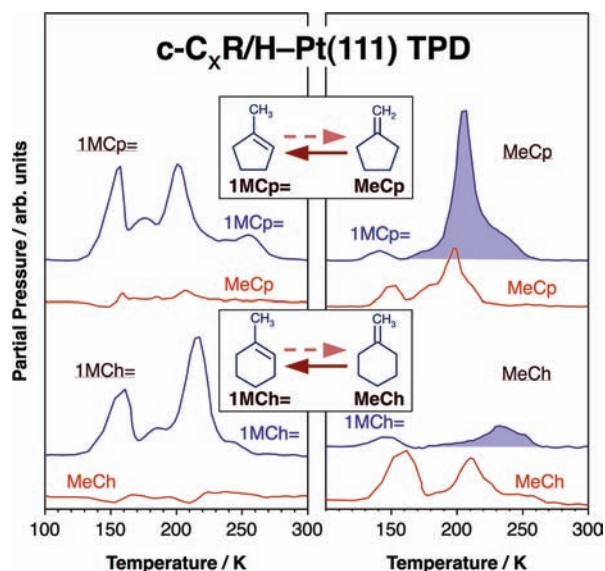
first step in that reaction is the incorporation of a hydrogen atom into one of the two carbons of the double bond in the alkene and the formation of an alkyl surface intermediate; the alkyl is then converted back to an alkene via a  $\beta$ -H elimination step. The thing to notice here is that since the alkyl intermediate may contain different types of  $\beta$  hydrogens, that is, since it may have hydrogens bonded to  $\beta$ -carbon atoms in different chemical environments, the  $\beta$ -H elimination may not necessarily involve the same hydrogen incorporated in the preceding half-hydrogenation step. If that is the case, a new molecule may be made.

One example of this type of isomerization is the migration of C=C bonds in cyclic compounds. Figure 3 summarizes the temperature-programmed desorption (TPD) data obtained for two systems involving C<sub>5</sub><sup>22</sup> and C<sub>6</sub><sup>23</sup> cyclic moieties, respectively. Both reactions show preferential migration of the double bond from the exo position into a carbon–carbon bond inside the cycle. This is because the outside carbon in the methylene group of both methylenecyclopentane and methylenecyclohexane is the easiest to hydrogenate, and because  $\beta$ -H elimination from an inner carbon in the ring of the resulting methylcyclopentyl and methylcyclohexyl surface intermediates, respectively, is favored over the reversal of the original hydrogenation step. The difference in the activation barriers of the two dehydrogenation pathways available to the methylcycloalkyl intermediate is only about 3 kcal/mol, but that is sufficient to obtain high selectivities toward the production of the methylcycloalkene.

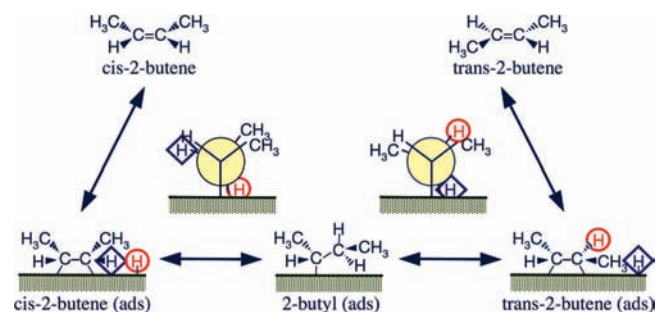
### 3. Stereoselectivity in Alkene Cis–Trans Isomerization

An even subtler example of selectivity involving  $\beta$ -H elimination from alkyl intermediates was identified in the cis–trans





**FIGURE 3.** Temperature-programmed desorption (TPD) data from studies on the regioselectivity of carbon-carbon double bond migration reactions on Pt(111) surfaces. Two examples, both involving cyclic compounds, are provided, namely, the interconversions between 1-methylcyclopentene (1MCp=) and methylenecyclopentane (MeCp) (top traces) and between 1-methylcyclohexene (1MCh=) and methylenecyclohexane (MeCh) (bottom traces). Traces are shown for the desorption of both compounds starting with surfaces covered with either the methylcycloalkenes (left panel) or the methylenecycloalkanes (right panel). In both cases, preferential migration is seen toward the former compounds, that is, toward migration of the double bond to a position within the cyclic moiety (shaded peaks).



**FIGURE 4.** Mechanism of the interconversion between the cis and trans isomers of 2-butene on metal surfaces. This reaction goes through a common 2-butyl intermediate and proceeds in a direction defined by the relative stereo restrictions imposed on the transition state of the two possible  $\beta$ -H elimination steps from that moiety (as indicated by the Newman projections in this figure).

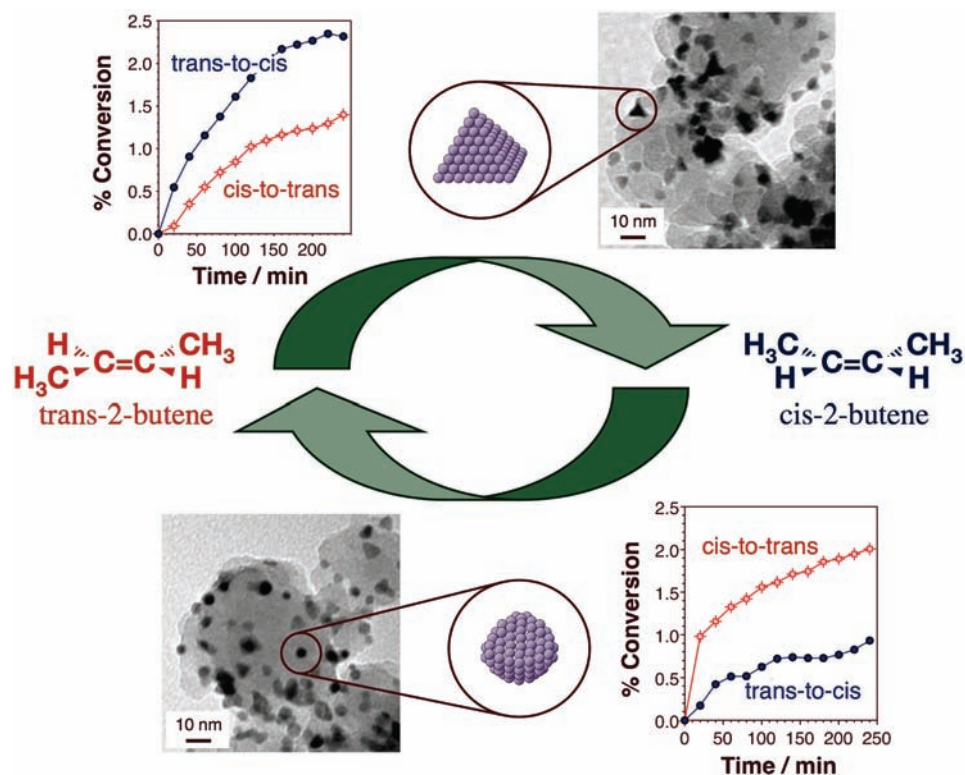
isomerization of C=C bonds in alkenes. The mechanism involved is illustrated, for the case of 2-butenes, in Figure 4. As in double-bond migrations, C=C cis-trans isomerizations require an alkene hydrogenation step and a subsequent  $\beta$ -H elimination from the resulting alkyl surface intermediate. However, here, the latter reaction always occurs at the same  $\beta$  carbon atom, also the same involved in the initial hydrogenation (the inner carbon not bonded to the surface). Selectivity, there-

fore, does not come from the regioselectivity of the dehydrogenation step, but rather from the steric differences in the configurations required to abstract the different hydrogens within the same  $\beta$  carbon atom. This is better illustrated by the Newman projections in Figure 4, where the two hydrogens bonded to the inner  $\beta$  carbon have been labeled with a red circle and a blue diamond, respectively: elimination of the red-circle hydrogen leads to the production of *cis*-2-butene, whereas elimination of the blue-diamond hydrogen results in the formation of *trans*-2-butene.

In our initial surface-science work on these systems, we found that on Pt(111) surfaces, *trans*-2-butene isomerizes preferentially to its *cis* counterpart.<sup>24–26</sup> That is a surprising result, not what is expected thermodynamically and also not what is commonly observed in catalytic processes. Certainly, significant amounts of *trans* fats are produced during the partial hydrogenation of edible oils, a fact that has gained national attention because of the associated adverse health effects.<sup>27</sup> This is because the catalytic hydrogenation of olefins is often accompanied by *cis*-*trans* isomerization reactions, since they both share the same surface alkyl intermediates. Natural oils are almost exclusively comprised of *cis*-olefins, but the fat obtained after their partial hydrogenation almost invariably contains a large fraction of (undesirable) *trans*-C=C double bonds.

A more detailed study of this system revealed a couple of key factors that affect selectivity in *cis*-*trans* conversions of alkenes. Perhaps first and foremost is the effect exerted by coadsorbed hydrogen. It had already been known that, in general, the presence of hydrogen on the surface of metals weakens the adsorption of alkenes and favors  $\pi$  adsorption rather than the di- $\sigma$  bonding that dominates on clean surfaces.<sup>28–30</sup> However, here we learned that, at least on Pt(111), this effect is stronger with *cis* than with *trans* alkenes. TPD experiments with 1,4-difluoro-2-butenes, where fluorine substitutions were used to label and differentiate between the *cis* and *trans* isomers, showed that the *trans* isomer is indeed the more stable of the two on the clean (hydrogen-free) Pt(111).<sup>31</sup> Direct studies with 2-butyl surface intermediates, prepared by activation of 2-halobutanes, also indicated the preferential production of *trans*-2-butene.<sup>26</sup> On the other hand, quantum mechanics (DFT) calculations clearly attested to both a switch from di- $\sigma$  adsorption on clean Pt(111) to  $\pi$  bonding on hydrogen-saturated surfaces and, more revealing, the reverse of relative stability from the *trans* to the *cis* isomer of the alkene.<sup>32</sup>

The DFT study also pointed to the role that the structure of the surface plays in determining the bonding strength of alkenes on metals, which appears to be due to, at least in part,



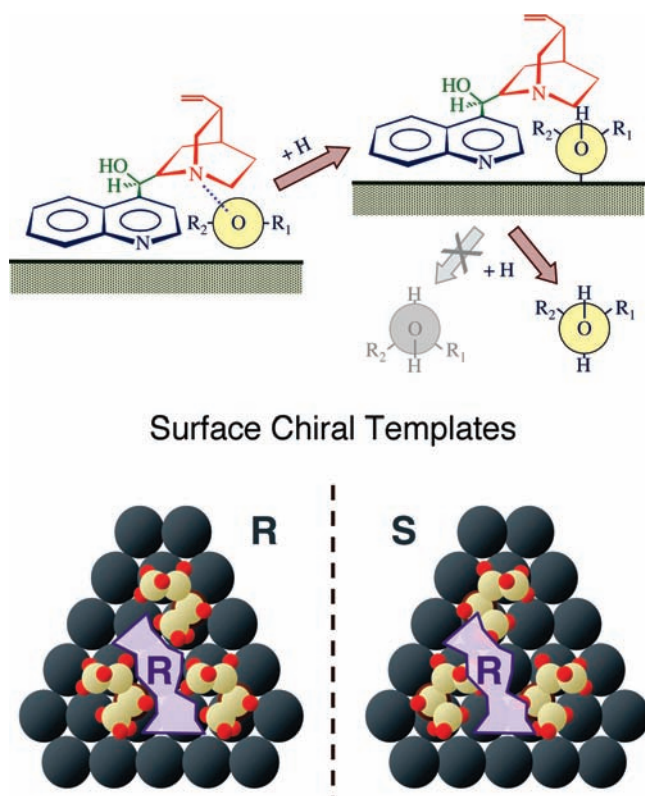
**FIGURE 5.** Kinetic catalytic data and transmission electron microscopy (TEM) images to indicate the correlation that exists between the structure of the surface of a platinum-based catalyst and its selectivity in alkene cis–trans isomerization conversions. Catalysts consisting of tetrahedral platinum particles, which only expose (111) facets promote the formation of the cis isomer preferentially (top). Other more round structures, conversely, display a reversed selectivity toward the trans isomer (bottom).

a significant reconstruction of the metal surface atoms induced by the adsorption.<sup>32</sup> It was hypothesized that such reconstruction may be driven by the need to minimize the steric interactions between the surface and the end groups of the alkene (which are expected to be more severe with the trans isomer), and that perhaps more open surfaces would require a lesser degree of reconstruction and therefore show the expected higher stability for the trans isomer. This was indeed corroborated experimentally, first by TPD using single-crystal surfaces with more open structures,<sup>33</sup> and later by using supported catalysts consisting of tetrahedral platinum particles, which only expose the (111) planes that promote cis alkene formation.<sup>33,34</sup> In the latter, kinetic measurements indicated that the tetrahedral Pt catalysts promote trans-to-cis isomerizations at a rate almost twice as high as they do similar trans-to-cis conversions, and also that the more rounded particles obtained by annealing to high temperatures show a preference for the reverse cis-to-trans reaction (Figure 5).<sup>33,34</sup> Here is a clear example where stereoselectivity in dehydrogenation steps involving hydrocarbon surface intermediates can be controlled by controlling the structure of the surface of the catalysts used.

#### 4. Enantioselectivity in Double-Bond Hydrogenation

There is yet one additional level of subtlety possible when considering selectivity in hydrogenation reactions with so-called prochiral molecules, that is, molecules that yield chiral products. Ketones with carbonyl moieties attached to two different groups, for instance, can be hydrogenated to chiral alcohols. Typically, that hydrogenation occurs with equal probability on both sides of the molecular plane and therefore results in the production of racemic mixtures. However, it has been shown that, in some instances, the addition of a chiral modifier promotes the preferential formation of one enantiomer over the other.<sup>35,36</sup> Such enantioselectivity in solid catalysts modified by chiral modifiers is attained by creating a chiral catalytic site on the surface.

The best example of this behavior is that of the hydrogenation of  $\alpha$ -ketoesters by platinum catalysts, where promotion with small amounts of cinchona alkaloids can lead to enantioselectivities in excess of 95%.<sup>35,37</sup> The proposed mechanism by which this enantioselectivity is attained is illustrated schematically at the top of Figure 6: the cinchona modifier forms a weak complex with the reactant and places the reactant within its chiral



**FIGURE 6.** Schematic illustration of the two main models by which chiral modifiers are proposed to bestow enantioselectivity to heterogeneous catalysts. (Top) Formation of one-to-one complexes between the modifier (cinchonidine) and the reactant. In this case, the carbonyl group of the reactant (shown as a Newman projection) is held by the adsorbed cinchonidine so it can only adopt one of its two possible orientations with respect to the surface and therefore incorporate hydrogen atoms on only one side of the molecule. (Bottom) Formation of supramolecular surface chiral templates, where three molecules of the enantiopure templating agents (2-butoxide adsorbates), either the (*R*) (left panel) or the (*S*) (right panel) forms, form a pocket of specific chirality on the surface. The (*R*) purple structure fits nicely in the chiral site left by the (*R*) butoxides but not on that defined by the (*S*) enantiomers.

pocket, forcing the carbonyl group to adopt a specific orientation with only one side of the molecular plane available for reaction once the cinchona binds to the metal surface. Hydrogenation of the carbonyl moiety then leads to the preferential formation of one of the two possible enantiomers of the alcohol. We have been probing the molecular details of the adsorption of cinchona alkaloids from solutions onto platinum surfaces that underpins this chemistry by using in situ reflection–absorption infrared spectroscopy (RAIRS).<sup>38–40</sup>

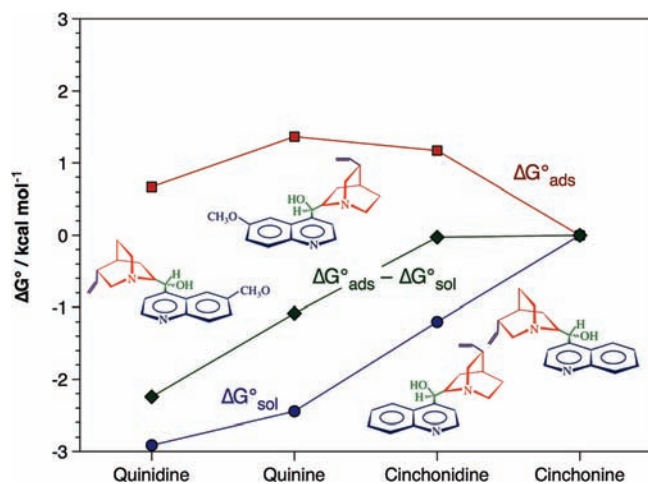
The first lesson that we have learned from our work in this area is that many of the kinetic trends reported for cinchona-modified catalytic systems can be explained by the details of the adsorption of the cinchona alkaloid on the platinum surface. For instance, it was found that the aromatic ring by which the cinchona bonds to the surface reorients from flat adsorp-

tion to a tilted configuration upon increasing the concentration of the chiral modifier in solution, and that this geometrical rearrangement explains the accompanying loss in enantioselectivity seen during  $\alpha$ -ketoester hydrogenation catalysis.<sup>41,42</sup> In a second study, it was shown that an initial pretreatment of the surface with hydrogen is needed to start both cinchona adsorption and catalytic conversions, and also that extensive hydrogen exposures lead to the hydrogenation of the chiral modifier and to a loss in catalytic activity and selectivity.<sup>43,44</sup> The choice of solvent was found to heavily influence both cinchona adsorption and its effectiveness in adding enantioselectivity to catalysts as well: solvents of intermediate polarity, roughly matching that of the cinchona alkaloids, typically perform best in both adsorption and catalytic experiments.<sup>45,46</sup>

Chiral modification of catalysts with cinchona alkaloids appears to require a fast adsorption–desorption equilibrium on the platinum surface. Our research indicates that the extent of that equilibrium is affected not only by the geometry of adsorption adopted by the cinchona alkaloids but also by their solubility in the solvent used.<sup>40,47</sup> A dramatic manifestation of the interplay between these two factors is seen when the adsorption behavior of closely related cinchona molecules is compared. For instance, although cinchonine adsorbs more strongly on Pt than its near-enantiomer cinchonidine,<sup>48</sup> cinchonidine can still displace cinchonine from the surface (the opposite not being possible),<sup>49</sup> and typically dominates chiral modification in catalysis. This is because cinchonine is also less soluble than cinchonidine: the energy gained by adsorption is compensated by an energy loss due to the decrease in solubility (Figure 7).

Differences in both adsorption energy and solubility across series of similar cinchona alkaloids as those reported in Figure 7 are likely to relate mainly to differences in bonding to the surface, but they also reflect more subtle effects related to the entropy of the system. Specifically, the presence of peripheral groups such as the vinyl group in the quinuclidine ring (and the methoxy in the quinoline moiety of quinine and quinidine) may reduce the rotational configuration space available to those molecules and with that their entropy. Notice in particular the difference in relative position of the vinyl moiety within the structures of quinine and cinchonidine, where it points up and away from the quinoline ring (in the drawings in Figures 6 and 7) versus the structures of quinidine and cinchonine, where it is placed down and closer to the aromatic ring. This results in differences in internal vibrational and rotational modes, and consequently in decreases in entropy of solution and solubility. Evidence from two-dimensional NMR, DFT calculations, and temperature-dependent solubility stud-



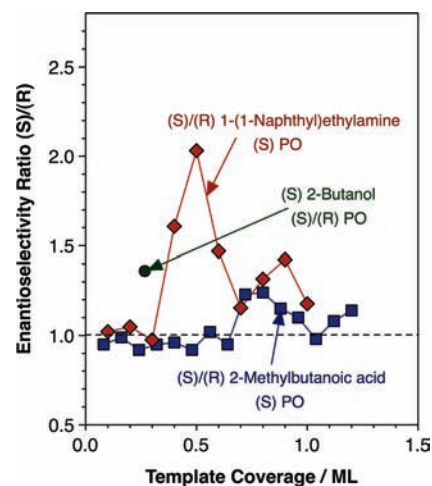


**FIGURE 7.** Relative Gibbs free energies for the solubility in  $\text{CCl}_4$  and for the adsorption on a platinum surface of four closely related cinchona alkaloids. As the structures provided in the figure show, the quinidine–quinine and cinchonidine–cinchonine pairs are near enantiomers, the former having an additional methoxy group in the quinoline ring. The differences in both solubility and adsorption observed within these four compounds can only be ascribed to an effect exerted by the peripheral groups, the methoxy and the vinyl moieties in the quinoline and quinuclidine rings, respectively.

ies support this conclusion.<sup>50,51</sup> The hypothesis of the central role that peripheral substituents play in defining the physical chemistry properties of cinchona alkaloids is one that we are exploring at present, because it provides a handle on how to tailor the adsorption properties of the cinchona at a molecular level and with that their chiral modification ability in catalysis.

Simpler molecules such as tartaric acid have also been shown to act as chiral modifiers in some heterogeneous catalytic hydrogenations.<sup>52</sup> In those cases, the surface is expected to play a more central role, helping form the required chiral site by assembling local supramolecular structures with chiral void spaces.<sup>53</sup> The bottom panel of Figure 6 illustrates how this may work with three 2-butoxide moieties, which adsorb on our hypothetical surface in a triangular fashion to create a chiral site of a specific handedness. The (*R*) purple shape in the diagram fits nicely within the pocket left by the three (*R*)-2-butoxide moieties (Figure 6, bottom, left), but not in the (mirror image) site produced by similarly arranged (*S*)-2-butoxide species (Figure 6, bottom, right).

This chiral templating of the surface can be probed indirectly by quantitatively contrasting the adsorption of a second chiral molecule on identical surfaces precovered with each of the two enantiomers of the modifier: any difference in uptake provides an indication of enantioselectivity.<sup>54</sup> In our studies, (*S*)- and (*R*)-propylene oxide (PO) were used to probe the templating capabilities of enantiopure 2-butoxide (pre-



**FIGURE 8.** Summary of TPD yield data obtained in chiral titration experiments using enantiopure propylene oxide (PO) highlighting the enantioselectivity imparted to the surface by three chiral modifiers, 2-butoxide, 2-methylbutanoic acid, and 1-(1-naphthyl)ethylamine. In all three cases, an enantiomeric excess is seen in the uptake of PO of the same chirality as the chiral modifier used within a specific range of coverages. This behavior can be explained by the model presented in Figure 6.

pared by thermal activation of adsorbed 2-butanol),<sup>55</sup> 2-methylbutanoic acid,<sup>56</sup> and 1-(1-naphthyl)ethylamine (NEA)<sup>57</sup> on Pt(111) surfaces. All three adsorbates display the behavior expected from chiral modifiers: the PO uptake is higher on surfaces pre dosed with templating agents of the same chirality (Figure 8). In addition, the reported enantioselectivity is seen only within a specific range of coverages of the chiral modifier on the surface, around 0.3 monolayers (ML) for 2-butoxide, 0.5 ML for 2-methylbutanoic acid, and 0.8 ML for NEA (Figure 8). This is to be expected, because a minimum coverage may be needed to get the neighboring adsorbates in close enough proximity to define a molecular-size chiral pocket and because high coverages may lead to blocking of the empty chiral sites. An enantioselectivity excess in the uptake of the probe molecule between the two enantiomeric surfaces only over a well-defined range of surface coverages is in fact one of the key observations used to argue for the chiral templating effect.<sup>40,58</sup>

The distinction between one-to-one reactant–modifier complex formation and supramolecular templating in the bestowing of enantioselectivity to surfaces by chiral modifiers is somewhat arbitrary; in reality, all cases may involve both mechanisms to different degrees. This is what has become evident in our studies with the three chiral modifiers reported in Figure 8. In the case of the butoxide groups, all the evidence, from RAIRS and TPD experiments, points to a dominant templating effect.<sup>55</sup> However, with 2-methylbutanoic acid, in addition to an increase in uptake, the PO molecule also binds with

a slightly higher energy on the homochiral surface.<sup>56</sup> The latter effect is particularly noticeable in the case of NEA, where two different PO adsorption sites with appreciably different binding energies are in fact clearly detected.<sup>57</sup> Actually, NEA is known to act as a single-molecule chiral modifier, in the style of cinchona alkaloids, in some catalytic hydrogenation processes.<sup>59</sup> The energetic contribution seen with NEA (and to a lesser extent with 2-methylbutanoic acid) can be ascribed to direct interactions between single modifier and probe (or reactant) molecules. It is most likely supplemented by entropic elements due to the local arrangement of the molecules on the surface, allowing for the formation of chiral ensembles or even to the interconversion among different molecular conformations within each individual chiral modifier molecule (as is the case with the cinchona alkaloids).<sup>40,47</sup>

## 5. Concluding Remarks

In the preceding sections, we have briefly summarized the most salient conclusions from our studies on selectivity in hydrocarbon conversion reactions on surfaces. Our examples illustrate the different degrees of subtleties that may be involved in the mechanisms of those. In terms of dehydrogenation reactions where hydrogen abstraction is to be considered from different positions within the hydrocarbon chain, selectivity may be achieved by tuning the electronic properties of the surface. Most transition metals are quite efficient at promoting dehydrogenation steps, but they do so at different relative rates from different positions in the carbon chain. Hence, nickel shows a distinct preference for hydrogen elimination from the  $\alpha$  position and typically facilitates subsequent C–C bond-breaking steps. Platinum, by contrast, promotes  $\gamma$ -H elimination competitively and therefore facilitates isomerization processes instead.

Regioselectivity in dehydrogenation can therefore be controlled by electronic tuning of the catalyst. The stereochemistry of hydrogen elimination steps, on the other hand, requires control of the structure of the surface instead. This is clearly the case in alkene isomerizations, where the hydrogens to be eliminated may all be bonded to carbon atoms at the same (or closely related) positions in the chain but where the interactions between auxiliary groups and the surface may direct a specific H abstraction. Our example of how cis-to-trans alkene isomerization reactions can be promoted on Pt(111) surfaces provides a dramatic illustration of this principle.

Finally, enantioselectivity imposes even more stringent conditions on the catalytic site. In the case of the hydrogenation of prochiral unsaturated hydrocarbons, for instance, what is required is the induction of a specific adsorption geometry for

the reactant on the surface. Such adsorption control is likely to require complex chiral structures, and, in lieu of the ability to prepare solid surfaces with such complexity (as may be done in homogeneous or enzymatic catalysts), a molecular chiral modifier, acting as a cocatalyst, may be used instead. Local chiral sites may then be assembled out of one or more of these chiral modifiers on the surface. Chirality may be mainly provided by the modifier itself, as is the case with cinchona alkaloids, but may also be built out of a supramolecular structure held in place by the underlying surface.

In general, it is clear that increasing demands on catalytic selectivity require designs of catalytic sites of increasing complexity. The demands on the catalytic site imposed by the required selectivity may be quite stringent but, thanks to new advances in both our understanding of reaction mechanisms and synthetic methodologies from self-assembly and nanotechnology, may now be met via the preparation of heterogeneous catalysts with well-defined electronic properties and structures.

*This research has been funded by grants from the U.S. National Science Foundation and the U.S. Department of Energy.*

---

## BIOGRAPHICAL INFORMATION

**Francisco Zaera** received his undergraduate degree from the Simón Bolívar University in Caracas, Venezuela, and his Ph.D. from the University of California, Berkeley, under the supervision of Prof. Gabor A. Somorjai. After a three-year stint as Assistant Chemist at the National Synchrotron Light Source of Brookhaven National Laboratory, in a joint appointment with Exxon Research Laboratories, in 1986, he became a faculty member at the University of California, Riverside, where he is presently a Full Professor of Chemistry. Prof. Zaera has held a number of professional offices and editorial positions and is presently a Senior Editor of *The Journal of Physical Chemistry*. He has been awarded several international awards, including the ACS George A. Olah and Arthur W. Adamson and the North American Catalysis Society Paul H. Emmett Awards. His research interests are in the areas of surface and materials chemistry and of heterogeneous catalysis, with particular emphasis on surface reaction kinetics and in situ spectroscopic characterization of surface species.

---

## FOOTNOTES

\*E-mail: zaera@ucr.edu.

---

## REFERENCES

- 1 Thomas, J. M.; Thomas, W. J. *Introduction to the Principles of Heterogeneous Catalysis*; Academic Press: London, 1967.
- 2 Zaera, F. Outstanding mechanistic questions in heterogeneous catalysis. *J. Phys. Chem. B* **2002**, *106*, 4043–4052.
- 3 Zaera, F. Kinetics of chemical reactions on solid surfaces: Deviations from conventional theory. *Acc. Chem. Res.* **2002**, *35*, 129–136.



- 4 Zaera, F. Selectivity in hydrocarbon catalytic reforming: A surface chemistry perspective. *Appl. Catal., A* **2002**, *229*, 75–91.
- 5 Zaera, F. Surface chemistry of hydrocarbon fragments on transition metals: Towards understanding catalytic processes. *Catal. Lett.* **2003**, *91*, 1–9.
- 6 Bond, G. C. *Metal-Catalysed Reactions of Hydrocarbons*; Springer: New York, 2005.
- 7 Zaera, F. Preparation and reactivity of alkyl groups adsorbed on metal surfaces. *Acc. Chem. Res.* **1992**, *25*, 260–265.
- 8 Zaera, F. An organometallic guide to the chemistry of hydrocarbon moieties on transition metal surfaces. *Chem. Rev.* **1995**, *95*, 2651–2693.
- 9 Ma, Z.; Zaera, F. Organic chemistry on solid surfaces. *Surf. Sci. Rep.* **2006**, *61*, 229–281.
- 10 Zaera, F. Direct observation of  $\beta$ -hydride elimination reactions on metal surfaces. *J. Am. Chem. Soc.* **1989**, *111*, 8744–8745.
- 11 Zaera, F. On the mechanism for the hydrogenation of olefins on transition-metal surfaces: The chemistry of ethylene on Pt(111). *Langmuir* **1996**, *12*, 88–94.
- 12 Zaera, F. Reversibility of C<sub>1</sub> hydrogenation–dehydrogenation reactions on platinum surfaces under vacuum. *Langmuir* **1991**, *7*, 1998–1999.
- 13 Tjandra, S.; Zaera, F. Methyl iodide thermal reactions when chemisorbed on Ni(100) surfaces. *Langmuir* **1992**, *8*, 2090–2097.
- 14 Jenks, C. J.; Bent, B. E.; Zaera, F. The chemistry of alkyl iodides on copper surfaces. 2. Influence of surface structure on reactivity. *J. Phys. Chem. B* **2000**, *104*, 3017–3027.
- 15 Loaiza, A.; Xu, M.; Zaera, F. On the mechanism of the H-D exchange reaction in ethane over platinum catalysts. *J. Catal.* **1996**, *159*, 127–139.
- 16 Zaera, F.; Tjandra, S.; Janssens, T. V. W. Selectivity among dehydrogenation steps for alkyl groups on metal surfaces: Comparison between nickel and platinum. *Langmuir* **1998**, *14*, 1320–1327.
- 17 Zaera, F.; Tjandra, S. The thermal chemistry of neopentyl iodide on Ni(100) surfaces: Selectivity between  $\alpha$ -C–H and  $\gamma$ -C–H and between C–H and C–C bond-scission steps in chemisorbed neopentyl moieties. *J. Am. Chem. Soc.* **1996**, *118*, 12738–12746.
- 18 Janssens, T. V. W.; Jin, G.; Zaera, F. Change in reaction pathway induced by deuteration: Thermal decomposition of neopentyl groups on Pt(111) surfaces. *J. Am. Chem. Soc.* **1997**, *119*, 1169–1170.
- 19 Janssens, T. V. W.; Zaera, F. Neopentyl iodide on Pt(111). II. Hydrogenation and H-D exchange. *Surf. Sci.* **2002**, *501*, 16–30.
- 20 Zaera, F. The surface chemistry of heterogeneous catalysis: Mechanisms, selectivity, and active sites. *Chem. Rec.* **2005**, *5*, 133–144.
- 21 Zaera, F. Probing catalytic reactions at surfaces. *Prog. Surf. Sci.* **2001**, *69*, 1–98.
- 22 Morales, R.; Zaera, F. Thermal chemistry of 1-methyl-1-cyclopentene and methylene cyclopentane on Pt(111) surfaces: Evidence for double-bond isomerization. *J. Phys. Chem. B* **2006**, *110*, 9650–9659.
- 23 Morales, R.; Zaera, F. Thermal chemistry of 1-methyl-1-cyclohexene and methylene cyclohexane on Pt(111) single crystal surfaces. *J. Phys. Chem. C* **2007**, *111*, 18367–18375.
- 24 Lee, I.; Zaera, F. Selectivity in platinum-catalyzed cis–trans carbon–carbon double-bond isomerization. *J. Am. Chem. Soc.* **2005**, *127*, 12174–12175.
- 25 Lee, I.; Zaera, F. Thermal chemistry of C<sub>4</sub> hydrocarbons on Pt(111): Mechanism for double-bond isomerization. *J. Phys. Chem. B* **2005**, *109*, 2745–2753.
- 26 Lee, I.; Zaera, F. Infrared spectroscopy characterization of the chemistry of C<sub>4</sub> hydrocarbons on Pt(111) single-crystal surfaces. *J. Phys. Chem. C* **2007**, *111*, 10062–10072.
- 27 Veldsink, J. W.; Bouma, M. J.; Schoon, N.-H.; Beenackers, A. A. C. M. Heterogeneous hydrogenation of vegetable oils: A literature review. *Catal. Rev. - Sci. Eng.* **1997**, *39*, 253–318.
- 28 Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A. Ethylene hydrogenation on Pt(111) monitored in situ at high pressures using sum frequency generation. *J. Am. Chem. Soc.* **1996**, *118*, 2942–2949.
- 29 Ötner, H.; Zaera, F. Isothermal kinetic measurements for the hydrogenation of ethylene on Pt(111) under vacuum: Significance of weakly bound species in the reaction mechanism. *J. Phys. Chem. B* **1997**, *101*, 396–408.
- 30 Zaera, F.; Chrysostomou, D. Propylene on Pt(111). II. Hydrogenation, dehydrogenation, and H-D exchange. *Surf. Sci.* **2000**, *457*, 89–108.
- 31 Lee, I.; Nguyen, M. K.; Morton, T. H.; Zaera, F. Thermal chemistry of 1,4-difluoro-2-butenes on Pt(111) single crystal surfaces. *J. Phys. Chem. C* **2008**, *112*, 14117–14123.
- 32 Delbecq, F.; Zaera, F. Origin of trans-to-cis isomerization selectivity in 2-butene adsorbed on Pt(111) single crystal surfaces: A DFT study. *J. Am. Chem. Soc.* **2008**, *130*, 14924–14925.
- 33 Lee, I.; Delbecq, F.; Morales, R.; Albitzer, M. A.; Zaera, F. Tuning selectivity in catalysis by controlling particle shape. *Nat. Mater.* **2009**, *8*, 132–138.
- 34 Lee, I.; Morales, R.; Albitzer, M. A.; Zaera, F. Synthesis of heterogeneous catalysts with well-shaped platinum particles to control reaction selectivity. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 15241–15246.
- 35 Mallat, T.; Orglmeister, E.; Baiker, A. Asymmetric catalysis at chiral metal surfaces. *Chem. Rev.* **2007**, *107*, 4863–4890.
- 36 Ma, Z.; Zaera, F. Chiral modification of catalytic surfaces. In *Design of Heterogeneous Catalysis: New Approaches Based on Synthesis, Characterization, and Modelling*; Ozkan, U. S., Ed.; Wiley-VCH: Weinheim, Germany, 2009; pp 113–140.
- 37 Orito, Y.; Imai, S.; Niwa, S. Asymmetric hydrogenation of  $\alpha$ -keto esters using a platinum-alumina catalyst modified with cinchona alkaloid. *Nippon Kagaku Kaishi* **1980**, 670–672.
- 38 Kubota, J.; Ma, Z.; Zaera, F. In-situ characterization of adsorbates in solid-liquid interfaces by reflection-absorption infrared spectroscopy. *Langmuir* **2003**, *19*, 3371–3376.
- 39 Chu, W.; LeBlanc, R. J.; Williams, C. T.; Kubota, J.; Zaera, F. Vibrational band assignments for the chiral modifier cinchonidine: Implications for surface studies. *J. Phys. Chem. B* **2003**, *107*, 14365–14373.
- 40 Zaera, F. Chiral modification of solid surfaces: A molecular view. *J. Phys. Chem. C* **2008**, *112*, 16196–16203.
- 41 Kubota, J.; Zaera, F. Adsorption geometry of modifiers as key in imparting chirality to platinum catalysts. *J. Am. Chem. Soc.* **2001**, *123*, 11115–11116.
- 42 Ferri, D.; Büergi, T. An in situ attenuated total reflection infrared study of a chiral catalytic solid-liquid interface: Cinchonidine adsorption on Pt. *J. Am. Chem. Soc.* **2001**, *123*, 12074–12084.
- 43 Bartók, M.; Szöllösi, G.; Balázsik, K.; Bartók, T. Heterogeneous asymmetric reactions Part 25. On the pretreatment and prehydrogenation of Pt-alumina catalyst in the hydrogenation of ethyl pyruvate. *J. Mol. Catal. A* **2002**, *177*, 299–305.
- 44 Ma, Z.; Kubota, J.; Zaera, F. The influence of dissolved gases on the adsorption of cinchonidine from solution onto a platinum surface: An in-situ infrared spectroscopy study. *J. Catal.* **2003**, *219*, 404–416.
- 45 Ma, Z.; Zaera, F. The role of the solvent in the adsorption–desorption equilibrium of cinchona alkaloids between solution and a platinum surface: Correlations among solvent polarity, cinchona solubility, and catalytic performance. *J. Phys. Chem. B* **2005**, *109*, 406–414.
- 46 Blaser, H. U.; Imhof, D.; Studer, M. Kinetic modeling of the ligand accelerated catalysis in the enantioselective hydrogenation of ethyl pyruvate: Influence of solvents, catalysts and additives. *Stud. Surf. Sci. Catal.* **1997**, *108*, 175–182.
- 47 Mink, L.; Ma, Z.; Olsen, R. A.; James, J. N.; Sholl, D. S.; Mueller, L. J.; Zaera, F. The physico-chemical properties of cinchona alkaloids responsible for their unique performance in chiral catalysis. *Top. Catal.* **2008**, *48*, 120–127.
- 48 Ma, Z.; Lee, I.; Zaera, F. Factors controlling adsorption equilibria from solution onto solid surfaces: The uptake of cinchona alkaloids on platinum surfaces. *J. Am. Chem. Soc.* **2007**, *129*, 16083–16090.
- 49 Ma, Z.; Zaera, F. Competitive chemisorption between pairs of cinchona alkaloids and related compounds from solution onto platinum surfaces. *J. Am. Chem. Soc.* **2006**, *128*, 16414–16415.
- 50 Zaera, F. Chiral modification of solid surfaces: A molecular level view. *J. Phys. Chem. C* **2008**, *112*, 16196–16203.
- 51 Lai, J.; Ma, Z.; Mink, L.; Mueller, L. J.; Zaera, F. Role of peripheral groups in determining cinchona alkaloid physical and chemical behavior. Manuscript in preparation.
- 52 Osawa, T.; Harada, T.; Tai, A. Enantio-differentiating hydrogenation of prochiral ketones over modified nickel. *Catal. Today* **1997**, *37*, 465–480.
- 53 Raval, R. Assembling molecular guidance systems for heterogeneous enantioselective catalysis. *CATTECH* **2001**, *5*, 12–28.
- 54 Stacchiola, D.; Burkholder, L.; Tysoe, W. T. Enantioselective chemisorption on a chirally modified surface in ultrahigh vacuum: Adsorption of propylene oxide on 2-butoxide-covered palladium(111). *J. Am. Chem. Soc.* **2002**, *124*, 8984–8989.
- 55 Lee, I.; Zaera, F. Enantioselectivity of adsorption sites created by chiral 2-butanol adsorbed on Pt(111) single-crystal surfaces. *J. Phys. Chem. B* **2005**, *109*, 12920–12926.
- 56 Lee, I.; Zaera, F. Chiral templating of surfaces: Adsorption of (S)-2-methylbutanoic acid on Pt(111) single-crystal surfaces. *J. Am. Chem. Soc.* **2006**, *128*, 8890–8898.
- 57 Lee, I.; Ma, Z.; Kaneko, S.; Zaera, F. 1-(1-Naphthyl)ethylamine adsorption on platinum surfaces: On the mechanism of chiral modification in catalysis. *J. Am. Chem. Soc.* **2008**, *130*, 14597–14604.
- 58 Stacchiola, D.; Burkholder, L.; Zheng, T.; Weinert, M.; Tysoe, W. T. Requirements for the formation of a chiral template. *J. Phys. Chem. B* **2005**, *109*, 851–856.
- 59 Minder, B.; Schuerch, M.; Mallat, T.; Baiker, A.; Heinz, T.; Pfaltz, A. Enantioselective hydrogenation of ethyl pyruvate over Pt/alumina modified by (R)-1-(1-naphthyl)ethylamine derivatives. *J. Catal.* **1996**, *160*, 261–268.