

## FEATURE ARTICLE

## Outstanding Mechanistic Questions in Heterogeneous Catalysis

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This Feature Article summarizes key results from our studies on the kinetics of chemical reactions on solid surfaces as they relate to heterogeneous catalysis. Emphasis is placed on the identification of specific issues of relevance to the design of catalytic processes, particularly the need for highly selective catalytic reactions. From the kinetic point of view, issues of selectivity translate into controlling relative activation energies within a small fraction of their absolute value. In the case of catalytic reforming of hydrocarbons, the nature of the final products is determined by the regioselectivity of an early dehydrogenation from surface alkyl intermediates (from the  $\alpha$ ,  $\beta$ , or  $\gamma$  position), a step greatly affected by the electronic structure of the metal used as catalyst. In the case of partial oxidation reactions, both the geometry of the local ensemble of surface atoms in the catalytic site and the presence of surface species such as hydroxide groups play determining roles in defining selectivity. A third factor is adsorption geometry, which often varies with changing reaction conditions: variations in concentration of the modifier in chiral catalysis, for example, may lead to dramatic changes in the enantioselectivity of hydrogenation processes. High pressures can induce new types of bonding between adsorbates and surfaces as well, opening new mechanistic routes for catalytic reactions: the hydrogenation of olefins, where  $\pi$  bonding occurs on top of strongly bonded carbonaceous deposits, falls into this category. Finally, the inhomogeneous distribution of adsorbates within the surface can be manifested in the formation of local islands, and those can promote specific catalytic reactions; witness, for instance, the effect of islanding on reactivity in the catalytic oxidation of carbon monoxide and during the catalytic reduction of nitrogen oxide.

## 1. Introduction

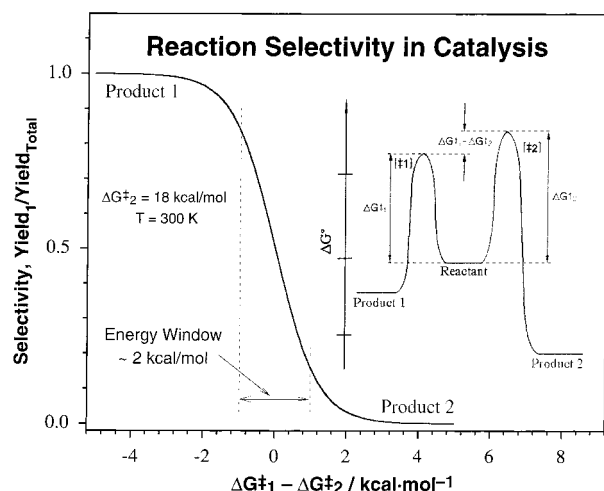
Although catalysis is a mature field, it remains at the center of most industrial processes, accounting for about a quarter of the world's gross domestic product.<sup>1</sup> The term catalyst was coined by Berzelius in 1835 to refer to substances that increase the rate of chemical reactions without being themselves consumed.<sup>2,3</sup> Berzelius' definition highlights the fact that, at the beginning at least, the focus of catalysis was placed on accelerating reaction rates. As more complex catalytic processes were developed, however, the emphasis shifted toward improving their selectivity. A reaction that is highly selective toward the desired product(s) is bound to consume less reactants, minimize the need for expensive and difficult separation processes, and create less polluting byproducts. A molecular-level control of the selectivity of catalysts is arguably the single most important challenge in this field for the future.

The success of catalysis relies on the ability of the catalyst to modify the kinetics of the chemical system being catalyzed. Specifically, a catalyst accelerates chemical reactions by opening alternative mechanisms with lower activation barriers.<sup>4</sup> According to transition state theory, the rate of any reaction is exponentially dependent on its activation energy, so small

decreases in the latter translate in significant increases in the former.<sup>5</sup> When considering selectivity, however, what matters is not so much the absolute height of the barrier toward the desired pathway, but its relative height compared to those of other undesirable side steps. This is illustrated in Figure 1, which shows how changes in the difference between the activation barriers of two competing reactions of a few kcal/mol, a small fraction of the absolute magnitude of each barrier, can lead to a complete switch in selectivity from one product to the other.

Consequently, controlling the relative heights of activation energy barriers in order to tune catalyst selectivity is a subtle and difficult task. Fortunately, many parameters can be varied to improve catalytic performance. In terms of the kinetics of catalysis, both entropic and enthalpic factors contribute to the overall activation barriers of catalytic reactions (hence our choice to represent those barriers in terms of Gibbs free energies in Figure 1) and can be varied to optimize catalytic activity and selectivity. From the experimental point of view, considerations need to be made about the catalyst itself (the materials to be used, the preparation methods, the use of supports and/or additives), the reactants (to choose the most feasible reactions, to facilitate reactions via molecular substitutions), and the conditions used (pressures, temperature, contact times). The combination of fundamental kinetic factors and experimental variables can be seen as the basis for a matrix with which to

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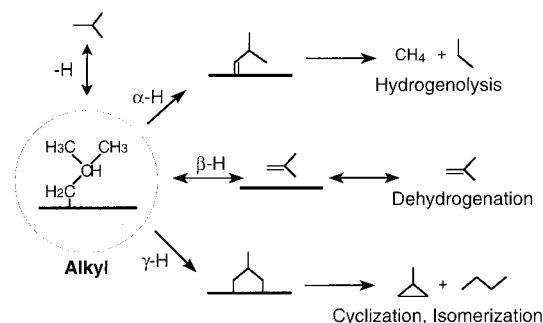
**Figure 1.** Illustration of the key role that relative heights among activation barriers for different reactions play in determining the selectivity of catalytic processes. The diagram on the right depicts a one-dimensional potential energy surface for the conversion of a reactant to two possible products. The rates of those reactions are determined by the absolute activation barriers, indicated here as  $\Delta G^\ddagger_1$  and  $\Delta G^\ddagger_2$ , but the selectivity between the two is controlled by the difference between those two values. The calculated selectivity of this two-reaction system, plotted as a function of  $\Delta G^\ddagger_1 - \Delta G^\ddagger_2$  in the left side of the figure, shows how a relative variation of about 10% in absolute barrier heights can lead to the switch in selectivity from the exclusive formation of one product to the other. We believe that being able to control selectivity is the main issue facing catalysis in the future.

guide our thinking during the design of catalytic processes. That, however, requires a better understanding of the underlying chemical principles behind catalytic reactions.

In this Feature Article, we elaborate on what we believe are some of the key issues limiting both our basic understanding of catalysis and the extension of that knowledge to the design of selective catalysts of practical use in industry. For one, it is not yet possible to predict reliably how the relative rates of similar reactions are affected by electronic changes in the catalyst. The resolution of this issue is central to the conversion of hydrocarbons, where the regioselectivity of dehydrogenation steps often defines the composition of the catalytic products. In addition, the nature of the catalytic site, its structure and chemical composition in particular, is also critical in determining selectivities in reactions such as partial oxidations. Control over the design of complex active sites and predictability of their behavior toward specific reactions is highly desirable. Last, the details of the chemical bonding between reactants and catalytic surfaces, including adsorption geometries, electronic interactions, and spatial distributions, have also proven of much relevance to a variety of processes associated with chiral catalysis and pollution abatement.

We in our laboratory have over the years focused on addressing the fundamental questions associated with the issues listed above. Our approach involves the characterization of surface intermediates and of the elementary steps they follow on well-defined surfaces, usually those of single crystals, under well-defined conditions, typically ultrahigh vacuum (UHV).<sup>6,7</sup> Our work, in conjunction with that of others, has greatly advanced the atomic-level understanding of catalysis, but has also generated new, still unresolved, problems. Here we present a personal view of the state of our knowledge of the surface chemistry of catalysis by pointing to some key recent developments as well as by introducing what we think are some of the most pressing pending quandaries in this area.

## Selectivity in Reforming via Regioselective Dehydrogenation



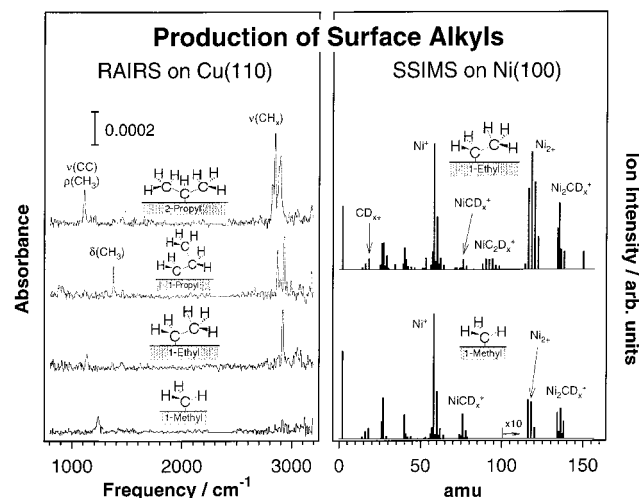
**Figure 2.** Schematic diagram of the reaction mechanism for the catalytic conversion of hydrocarbons on transition metal surfaces. Isobutane is used here as a prototypical example of the alkanes main components in crude oil. Also, the mechanism depicted in this figure is drawn to emphasize the steps relevant to the reforming of the raw feedstock to high-octane gasoline. The rate-limiting step in these processes is the initial C–H bond activation that yields alkyl surface intermediates (*sec*-butyl in this case), but the selectivity of the overall process is defined by the regioselectivity of the subsequent dehydrogenation reaction. It is our contention that  $\beta$ -hydride elimination typically dominates the chemistry of adsorbed alkyl groups, but that it is the relative rates between the  $\gamma$ - and  $\alpha$ -H elimination steps that determines the selectivity between the desirable cyclization and isomerization reactions and the undesirable hydrogenolysis, respectively.<sup>7,13</sup>

## 2. Selectivity in Hydrocarbon Conversion

One example where the selectivity of the catalyst determines the viability of the industrial process is hydrocarbon reforming.<sup>8,9</sup> When applied to the oil industry, reforming refers to the reconstruction of gasoline-range molecules to improve the quality of the fuel (as measured by its octane number).<sup>10</sup> Reforming processes involve many reactions, including hydrogenation–dehydrogenation, isomerization, cyclization, and aromatization steps, and therefore require particularly selective catalysts. From its introduction by the Universal Oil Products Company in 1949,<sup>11</sup> platinum has been the basic element used in reforming catalysis, and despite the extensive research carried out since, no cheaper alternatives have been found to date. The need to use platinum for reforming comes from the fact that, although many transition metals promote key hydrocarbon hydrogenation reactions, only platinum-based catalysts favor the selective production of reforming products. Nickel, for instance, promotes undesirable cracking instead. The electronic structure of the metal greatly influences the relative rates of the relevant surface reactions.

Typically, the step that determines the overall rate of reforming is the initial activation of the saturated hydrocarbons that comprise most of the fraction of crude oil used for gasoline production. On the other hand, the selectivity toward high-octane products is defined not by that rate-limiting step, but by the surface reactions followed by the surface alkyl intermediates resulting from such first step. It is our contention that it is the regioselectivity of the second dehydrogenation step, a hydride elimination from the alkyl intermediate in the terminology of organometallic chemistry,<sup>12</sup> that determines the identity of the final products (Figure 2).<sup>13,14</sup> To better understand this issue of selectivity in reforming, we some years ago embarked on a detailed characterization of the chemistry of alkyl species on transition metal single-crystal surfaces.<sup>12,15–28</sup>

Our first task in this endeavor was to find alternative routes for the preparation of surface hydrocarbon species in order to

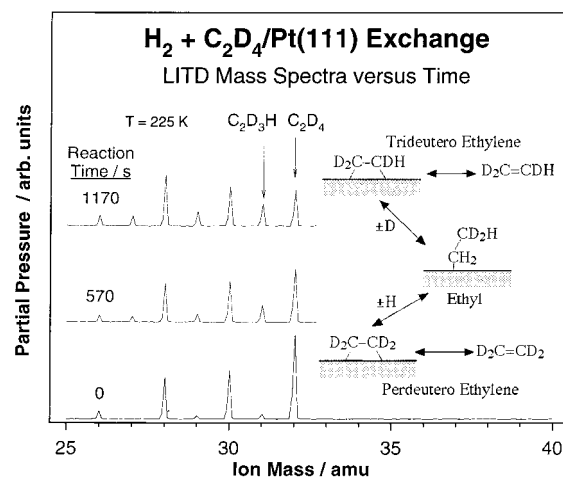


**Figure 3.** Examples of the spectroscopic evidence gathered in our group for the formation of alkyl surface moieties after thermal activation of adsorbed alkyl halide precursors. The left panel displays infrared (RAIRS) spectra for the methyl, ethyl, and 1- and 2-propyl groups that form after annealing the corresponding alkyl iodides on a Cu(110) single-crystal surface at approximately 200 K.<sup>22,27</sup> The right frame reports secondary ion mass spectrometry (SSIMS) data corroborating similar chemistry for methyl and ethyl iodides on Ni(100).<sup>20,23</sup> The thermal activation of adsorbed halo hydrocarbons has become a general and widely used approach for the preparation of hydrocarbon surface intermediates.<sup>21</sup>

bypass the difficulty of activating alkanes under UHV. Several procedures had been proposed in the past for this,<sup>21,29</sup> but our use of halo hydrocarbon precursors proved to be the most promising, and has become the most widespread.<sup>15,21,24,25,28</sup> We have shown that the cleavage of the carbon–halogen bonds in alkyl halides adsorbed on metal surfaces is quite facile<sup>30,31</sup> and that it leads to the formation of the desired hydrocarbon moieties (Figure 3).<sup>15,18,22</sup> It has also been proven that the adsorbed halide byproduct of this process does not affect the subsequent chemistry of the adsorbed hydrocarbon fragments in any significant way.<sup>7,13,21,32</sup> The activation of chemisorbed halo hydrocarbon precursors was first used to produce alkyl surface intermediates but has now been successfully extended to the production of surface carbenes,<sup>33–36</sup> vinyls,<sup>37,38</sup> allyls,<sup>39–42</sup> metallocycles,<sup>43–47</sup> and oxametallocycles,<sup>48,49</sup> among others.

Once the problem of how to prepare alkyl groups cleanly on single-crystal metal surfaces was solved, the thermal chemistry of those species could be characterized in detail. It soon became clear that such chemistry is dominated by the elimination of a hydrogen atom from the  $\beta$  position, that is, from the carbon adjacent to that bonded to the surface (Figure 2).<sup>12,24,29,50</sup> One of the earliest indications of the occurrence of this step came from temperature-programmed desorption (TPD) studies on the decomposition of deuterium-labeled ethyl iodides on Pt(111),<sup>51</sup> but more direct evidence is now available in the form of the detection of the resulting olefin.<sup>19,26,34,50,52</sup> The predominance of  $\beta$ -hydride elimination in adsorbed alkyls parallels similar chemistry with organometallic compounds, an analogy that extends to other reactions and that suggests that many hydrocarbon surface reactions are quite localized.<sup>7,12,53,54</sup>

$\beta$ -Hydride elimination explains directly the rapid equilibrium often established between alkanes and olefins in reforming reactions.<sup>55,56</sup> Together with the reverse C=C double-bond insertion into metal–hydrogen bonds (the half hydrogenation of adsorbed olefins to alkyls) and the reductive elimination between alkyl and hydrogen adsorbates (the second hydrogenation step of alkyls to alkanes), it also accounts for other catalytic

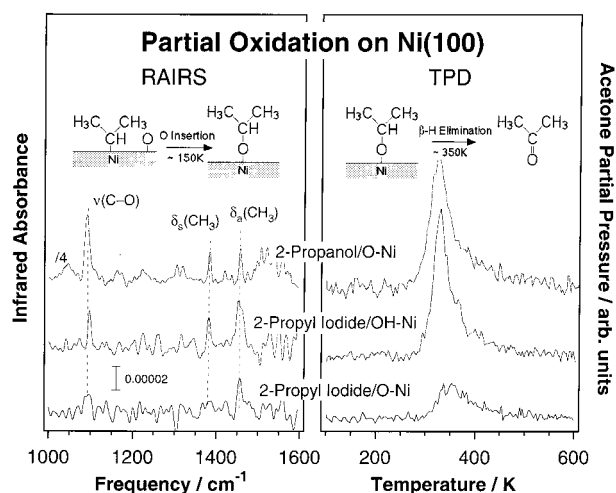


**Figure 4.** Laser-induced thermal desorption (LITD) spectroscopic data for isotopic scrambling in normal ethylene when coadsorbed with deuterium atoms on a Pt(111) single-crystal surface.<sup>67</sup> Extensive H–D exchange is seen in this system at temperatures as low as 225 K, as indicated by the growth of the peak at 31 amu representative of the formation of C<sub>2</sub>H<sub>3</sub>D after 500–1000 s of reaction. This isotopic exchange can be explained by a mechanism involving a  $\beta$ -hydride elimination step together with the reverse C=C double bond insertion into a Pt–H bond (the half hydrogenation of ethylene to ethyl), as indicated in the diagram on the right.<sup>56,57</sup>

processes such as double-bond migration and H–D exchange (Figure 4).<sup>17,26,33,39,42,43,56–68</sup> On the other hand, additional dehydrogenation steps are required to explain more demanding reforming processes. In particular, dehydrogenation at the  $\alpha$  position is likely to eventually lead to the scission of C–C bonds (the undesirable hydrogenolysis pathway),<sup>69</sup> while reactivity at the  $\gamma$  carbon may be responsible for desirable isomerization and cyclization steps instead (Figure 2).<sup>70–73</sup>

Hydride elimination from the  $\alpha$  and  $\gamma$  positions has certainly proven much less favored than dehydrogenation from the  $\beta$  carbon. They can nevertheless be probed by using adsorbates with no  $\beta$  hydrogens such as methyl, neopentyl, and benzyl moieties. The simplest example of  $\alpha$ -H elimination is the conversion of methyl to methylene, a reaction first established on Pt(111) by reflection–absorption infrared spectroscopy.<sup>18</sup> The multiple H–D exchange seen for methyl groups on Pt(111) suggested an activation barrier of about 10 kcal/mol for the initial  $\alpha$  dehydrogenation from those moieties,<sup>60,74</sup> approximately 2 kcal/mol higher than that for  $\beta$ -hydride elimination. This difference in activation energy between dehydrogenation from the  $\alpha$  and  $\beta$  positions was corroborated by additional indirect studies involving isotope scrambling during high-temperature ethylidyne formation,<sup>75</sup> and by catalytic H–D exchange experiments with ethane over platinum surfaces.<sup>65</sup> In the case of the thermal activation of methyl iodide on either Ni(100) or Ni(111) surfaces, the results are also consistent with  $\alpha$ -hydride elimination having a barrier  $\sim 2$  kcal/mol higher than that for  $\beta$ -hydride elimination from ethyl groups.<sup>20,33,62,76</sup>

Hydrogenolysis after  $\alpha$ -hydride elimination has been directly observed in the case of neopentyl iodide conversion on Ni(100), where isobutene production is detected at about 350 K.<sup>77,78</sup> In fact,  $\alpha$ -hydride elimination seems to dominate the overall chemistry on that surface, since no indication of  $\gamma$ -elimination can be seen at all. Interestingly, the initial elimination of one of the  $\alpha$  hydrogen atoms from the neopentyl moieties to produce neopentylidene intermediates occurs at much lower temperatures, below 200 K. This indicates that, even though the hydrogenolysis of alkyl intermediates may be rate limited by the C–C bond breaking step, it is decided by a much earlier



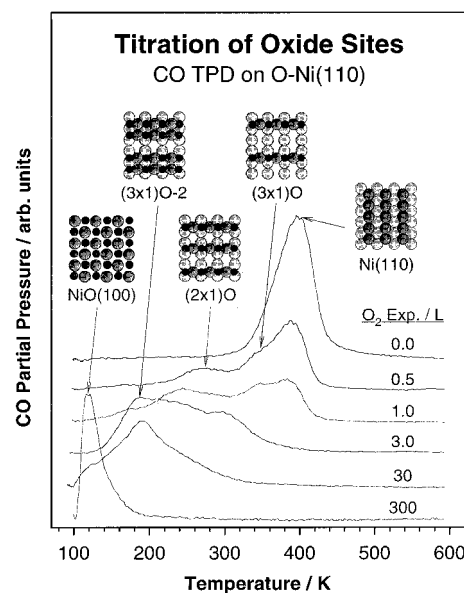
**Figure 5.** Evidence for the two-step mechanism responsible for the oxidation of 2-propyl groups to acetone on an oxygen-treated Ni(100) single-crystal surface. The left panel provides RAIRS data highlighting the early insertion of an oxygen atom into the metal–carbon bond to form an alkoxide intermediate; notice in particular the development of the C–O stretching vibration in the lower trace about 1100  $\text{cm}^{-1}$ .<sup>92</sup> The production of acetone at a later stage is indicated by its desorption around 350 K, as seen in the temperature programmed desorption (TPD) traces on the right.<sup>89</sup> This figure also highlights the fact that the partial oxidation reaction can be enhanced by the prior deposition of hydroxide groups on the surface; notice in particular the increase in signal intensities in the infrared bands as well as the larger yield of the desorbing acetone obtained in the TPD experiments observed in the middle traces. The corresponding data for 2-propanol is provided at the top to illustrate the similar chemistry followed by the adsorbed alkyls and alcohols, an observation that suggests that both react via the formation of the same alkoxide intermediate.

and facile  $\alpha$  dehydrogenation reaction. The story on platinum is quite different, because on that catalyst both  $\alpha$ - and  $\gamma$ -hydride eliminations take place at comparable rates.<sup>79–82</sup> It is this trend what explains the unique ability of platinum (as opposed to nickel, for instance) to catalyze reforming processes.<sup>43</sup>

### 3. Surface Sites for Partial Oxidation

In the previous example, selectivity was determined by the nature of the main element of the catalyst, which controls the relative reactivity of the different carbon atoms along the chain of the adsorbed hydrocarbon fragments. Sometimes it is the specific characteristics of the reaction site, things such as surface structure, that matter. This has been seen, for instance, in the synthesis of ammonia, where so-called  $\text{C}_7$  sites are required to activate the initial nitrogen molecule.<sup>83–85</sup> In fact, hydrocarbon reforming is another of a large number of processes known to be strongly affected by the structure of the surface of the catalyst.<sup>86–88</sup> More subtle properties of those surfaces may also exert some influence on catalytic processes involving complex materials such as alloys or oxides. This is indeed the case in partial oxidation reactions, as discussed next.

The expected thermodynamic products of reactions with hydrocarbons and oxygen are carbon dioxide and water. Under proper kinetic control, however, catalytic processes can be designed to yield useful oxygenated compounds instead. In one example from our work, the thermal activation of alkyl groups coadsorbed with oxygen on nickel surfaces results in the production of aldehydes or ketones (acetone when starting from 2-propyl).<sup>89–92</sup> This reaction was determined to take place in two steps, an initial facile insertion of an oxygen atom into the metal–carbon bond to produce an alkoxide intermediate, and a

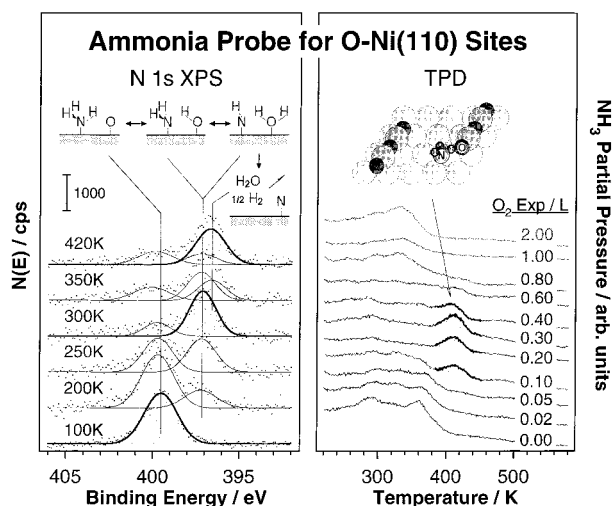


**Figure 6.** CO titration of local adsorption sites on a Ni(110) single-crystal surface treated with different amounts of oxygen.<sup>93</sup> The different peaks in the resulting CO TPD traces are indicative of different adsorption strengths, going from approximately 30 kcal/mol on clean nickel (the 400 K peak) to less than 10 kcal/mol in the case of NiO (the feature about 120 K). The five adsorption states detected in this experiments can be directly identified with different coordination numbers of oxygen atoms around the nickel adsorption sites based on the known structures for this O–Ni(110) system. The establishment of correlations between the formation of different O–Ni sites and the selective reactivity toward specific reactions (like the partial oxidation of alkanes illustrated in the previous figure) can aid in the design of better catalysts.

subsequent rate limiting  $\beta$ -hydride elimination of that alkoxide to the ketone (Figure 5). A particularly interesting observation from our studies is the detection of partial oxidation products only at intermediate oxygen surface coverages: too little oxygen and the reaction cannot proceed; too much and the nickel surface becomes fully oxidized and therefore nonreactive toward the alkyl groups. This change in behavior with degree of surface oxidation can be correlated to the local environment around the nickel atoms, the number of adjacent oxygen atoms in particular, as indicated by titration experiments with CO (Figure 6).<sup>93</sup> An appropriate, relatively small, ensemble of nickel and oxygen atoms is required to optimize the partial oxidation reaction.

The presence of hydroxide groups on the surface also enhances the partial oxidation pathway (Figure 5).<sup>90,91</sup> The role of OH surface groups in catalysis has, in our opinion, been underestimated, in particular given that they are almost always present in reactions involving water (as is the case here, where  $\text{H}_2\text{O}$  is one of the main byproducts). The presence of surface hydroxide groups not only leads to an enhancement of the yield for acetone production from partial oxidation of 2-propyl groups, but also facilitates the formation of acetaldehyde from ethyl moieties, a reaction not observed with oxygen alone.<sup>90,91</sup> It is not yet clear to us why this is, but the present evidence suggests that OH groups may mainly help the oxygen insertion step. To expand on this idea, the acidity and H–D exchange capacity of surface OH species can be tested independently by using appropriate probe molecules such as ammonia (Figure 7).<sup>92,94</sup> Again, it can be seen that metal surfaces with intermediate oxygen/OH coverages, representative of defective oxides, display unique chemistry.<sup>95–97</sup> Ultimately, changes in surface acidity can significantly modify the selectivity of oxidation catalysts. In the case of alcohol oxidation, for example, basic





**Figure 7.** Evidence for the presence of highly reactive oxygen atoms toward ammonia activation on partially oxidized Ni(110) surfaces. Ammonia is used here as a probe for the acidity and hydrogen exchange ability of surface sites.<sup>94,95</sup> Left panel: sequence of N 1s X-ray photoelectron spectroscopy (XPS) data obtained for ammonia co-adsorbed with oxygen as a function of temperature to illustrate the facile interchange of hydrogen atoms between the two species. Rapid interconversion between ammonia and water is attained via the formation of  $\text{NH}_2$ ,  $\text{NH}$ , and  $\text{OH}$  surface intermediates. Right panel: sequence of TPD traces for ammonia desorption from Ni(110) surfaces treated with different amounts of oxygen. A new high-temperature state is seen above 400 K at the intermediate oxygen doses associated with O atoms at the end of O–Ni–O surface chains (see diagram). These oxygen atoms are believed to be particularly active toward the abstraction of hydrogen atoms from adsorbed ammonia, the step responsible for the reactions indicated on the left panel. These experiments exemplify the importance of specific local ensembles of surface atoms in defining sites for selective catalysis.

oxides promote  $\beta$ -H dehydrogenation to aldehydes or ketones (the same as with alkyls), but acidic oxides enhance dehydration to olefins instead.<sup>91,98–100</sup>

#### 4. Adsorption Geometry

A third aspect of surface chemistry to be considered when discussing catalytic selectivity is the geometry of the adsorbed molecules. The reactivity of specific bonds in chemisorbed molecules depends on their degree of interaction with the surface, and that in turn correlates with the degree of proximity between the reacting moieties and the substrate.<sup>6</sup> An example of this is provided by what is known about the adsorption of carbon monoxide on metal surfaces. In most cases CO molecules adsorb with their axis perpendicular to the surface, with the carbon atoms pointing down in either atop, 2-fold bridged, or 3- or 4-fold nested positions.<sup>101</sup> However, a unique tilted CO adsorption geometry has been observed in a few instances, concretely in the cases of Cr(110),<sup>102</sup> Fe(100),<sup>103</sup> and Mo(100).<sup>104,105</sup> This tilted carbon monoxide state is particularly interesting from the point of view of catalysis, because it displays both a low C–O stretching frequency and an unusually long C–O bond, suggesting that it could be the precursor to dissociation in processes such as methanation and Fischer Tropsch synthesis.

In contrast to considerations associated with the nature of the catalyst or the surface site, adsorbate geometries are difficult to control, and therefore not so useful for designing new, more selective catalytic processes. Nevertheless, changes in adsorption geometry do occur, in particular as the density of the adsorbates on the surface is varied. For instance, aromatic compounds such as benzene tend to lie flat on transition metals at low coverages

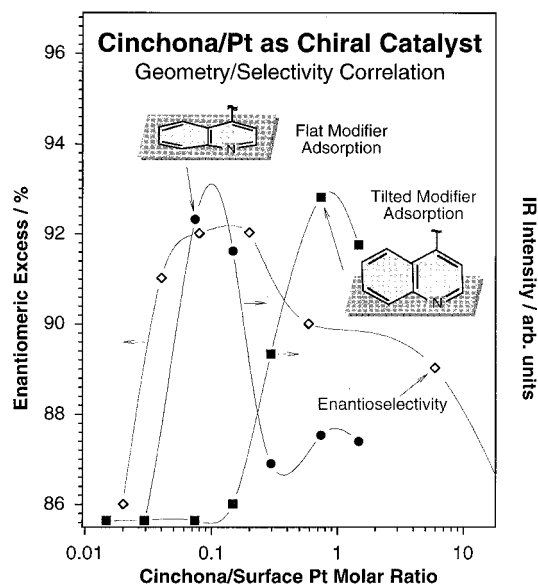
(in order to maximize the interaction between their  $\pi$  electrons and the conduction band of the substrate) but to rearrange into a stacked configuration at higher coverages (presumably to make room for more molecules and to take advantage of the interactions among the different aromatic rings).<sup>106,107</sup> Reorientation induced by surface crowding has also been reported for alkyl<sup>27,108</sup> and alkoxide<sup>109</sup> groups. Adsorption geometries may additionally be affected by the structure of the surface, as in the case of ethylene on copper, where the flat geometry seen on most metals<sup>12,56,110–112</sup> is observed on Cu(111)<sup>113</sup> and Cu(100)<sup>114</sup> but not on Cu(110).<sup>115,116</sup> In some cases, it has been possible to correlate structure directly with variations in reactivity and/or selectivity.

A particularly exciting illustration of the potential use of adsorption geometries to control reaction selectivities can be found in chiral catalysis. The production of optically pure compounds, a critical requirement in many pharmaceutical applications, requires the addition of enantioselectivity to the appropriate catalyst. Most of the catalytic synthesis of chiral molecules is presently done homogeneously<sup>117</sup> but could in principle be performed more efficiently by using heterogeneous systems. One way to impart chirality to a regular solid catalyst is by modifying its surface via the adsorption of a chiral molecule.<sup>118</sup> In one of the most publicized examples of this,  $\alpha$ -keto esters have been shown to selectively hydrogenate to one of the two possible  $\alpha$ -hydroxy ester enantiomers on supported platinum catalysts modified with cinchona alkaloids.<sup>119</sup> Interestingly, it has been reported that the enantioselectivity of that reaction depends on the concentration of the modifier in the reacting mixture.<sup>120</sup> Recent infrared spectroscopy experiments in our laboratory have shown that this is so because of an accompanying change in adsorption geometry (Figure 8).<sup>121</sup> It is clear that, in some systems, the selectivity of the catalyst can be optimized via the control of the concentration of the reactants (or the modifier, as in this case).

#### 5. Coverage Dependence

Variations in the coverages of the reactants on the surface of the catalyst can promote more profound changes on its chemistry, beyond simple changes in adsorption geometry. For instance, they can directly alter relative reaction rates, in particular in cases involving competition between unimolecular and bimolecular steps. With hydrocarbon species in particular, the coadsorption of hydrogen can be used to enhance hydrogenation (reductive elimination) pathways at the expense of dehydrogenation (hydride elimination) reactions,<sup>12,32,33,39,61,64,122,123</sup> and the use of deuterium can be employed to add isotope scrambling.<sup>60,63,65,67,81</sup> Catalytic selectivities can in fact change even if the ratio of the reactants in the reaction mixture is maintained constant. One classic surface-science example for this is that of the conversion of cyclohexene with hydrogen on Pt(111), where the almost exclusive production of benzene at pressures below  $10^{-4}$  Torr switches to the predominant formation of cyclohexane above 1 Torr.<sup>124</sup>

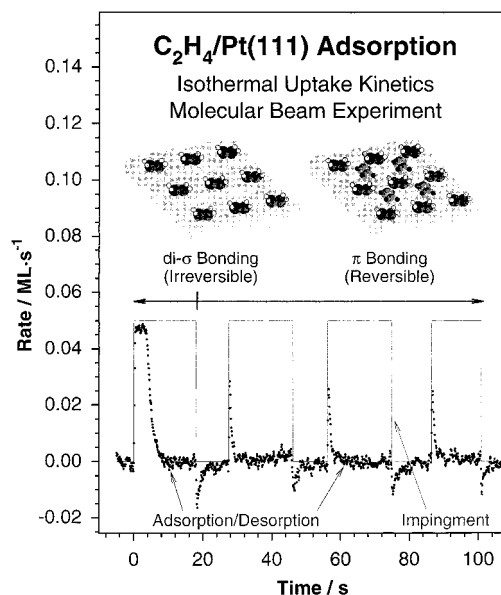
Our understanding of much of the hydrocarbon catalysis used in industrial applications is complicated further by the fact that those reactions involve metals covered with strongly bonded carbon-containing residues.<sup>86,125,126</sup> This carbonaceous layer is deposited on the surface in the early stages of the catalytic process because of the thermal decomposition of the unsaturated hydrocarbons produced by hydride eliminations from alkyl and other intermediates. In the case of olefins, the end products are alkylidyne species,<sup>56,127–131</sup> most likely the result of dehydrogenation of alkylidene intermediates.<sup>75,132–134</sup> Some indirect



**Figure 8.** Experimental data pointing to a correlation between the adsorption geometry of adsorbates and the selectivity of catalytic processes. This example corresponds to the enantioselective hydrogenation of ethyl pyruvate by a platinum catalyst modified with a chiral cinchona alkaloid. Infrared spectroscopy experiments on a platinum foil have indicated that there are three distinct regimes for the modifier depending on its concentration in the liquid solution: below 5% of saturation, where no discernible adsorption is detected, between 5 and 20%, at which point a few weak vibrational features are seen for a flat-lying bonded cinchonidine on the surface, and above 20%, when a complex infrared spectra corresponding to a tilted configuration is obtained.<sup>121</sup> In this figure a comparison is made between the evolution of the signal intensities for the infrared features at 1217 (flat adsorption, filled circles) and 1512  $\text{cm}^{-1}$  (tilted geometry, filled squares) as a function of cinchonidine concentration in the carbon tetrachloride solution, and the activity of a comparable catalytic system, a supported platinum catalyst modified with 10,11-dihydrocinchonidine (open diamonds).<sup>120</sup> Notice in particular the excellent correlation between the changes in the adsorption geometry of the modifier and the reported changes in activity and enantioselectivity of the catalyst: enantioselectivity is optimized by flat adsorption of the aromatic ring of the chiral modifier.

evidence suggests that alkylidynes may be directly involved in demanding reactions such as hydrogenolysis and reforming.<sup>65,135</sup> During the mild catalytic processes associated with hydrogenation of olefins and other multiple bonds, however, the strongly bonded carbonaceous species are likely to play only an indirect role, tempering the high activity of the clean metals, and perhaps also storing hydrogen to facilitate its transfer.<sup>56,126,136,137</sup>

The net result from the deposition of carbonaceous species during catalysis is that they modify the chemisorption characteristics of the reactants during reforming reactions. This is particularly true for the hydrogenation of unsaturated hydrocarbons, where new  $\pi$  bonding states develop (Figure 9). Olefin  $\pi$  bonding has been identified by vibrational spectroscopy, both under vacuum<sup>138</sup> and in situ under reaction conditions,<sup>116,139–141</sup> and molecular beam kinetic work has revealed that the  $\pi$ -bonded species are the ones directly involved in the hydrogenation process.<sup>66</sup> It has also become apparent that the rate-limiting step of the overall catalytic hydrogenation, the dissociative adsorption of hydrogen on the surface, is inhibited by the strongly adsorbed carbonaceous deposits. To improve the performance of hydrogenation catalysts, a balance needs to be reached between the two main effects exerted by the carbonaceous deposits, namely, the desirable passivation of hydrocarbon decomposition reactions, and the undesirable blocking of sites for hydrogen



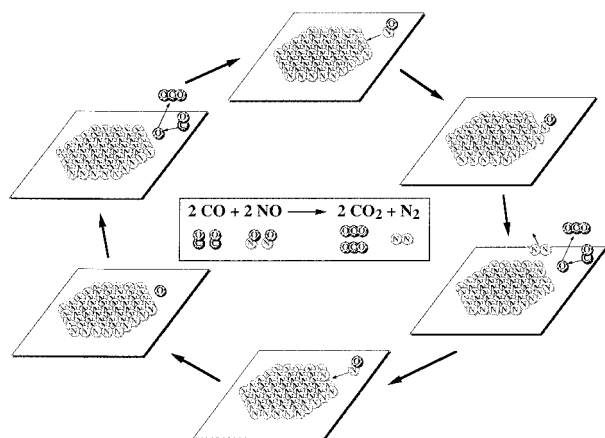
**Figure 9.** Typical isothermal kinetic data obtained for the uptake of ethylene on Pt(111) at 270 K by using a molecular beam technique.<sup>66</sup> The initial uptake of ethylene seen within the first 20 s of the experiment is followed by an additional small reversible adsorption of weakly ( $\pi$ ) bonded olefin, as manifested by the spikes observed right after blocking and unblocking of the beam. A comparison between the coverages of the strongly (di- $\sigma$ ) and weakly ( $\pi$ ) bonded ethylene and the initial rate of ethane formation indicate that it is the latter weakly adsorbed ethylene that is involved in the hydrogenation reaction. The formation of analogous  $\pi$  species in the case of propylene has also been directly determined by infrared spectroscopy.<sup>138</sup> The catalytic conversion of olefins on supported metal catalysts is believed to involve a similar  $\pi$  adsorption on top of strongly adsorbed carbonaceous deposits.<sup>14,32,122,127</sup>

adsorption. This is typically achieved by using alloys<sup>142,143</sup> and/or additives such as sulfur, alkaline metals, and chlorine.<sup>8,144</sup> In fact, alloys and additives are used extensively to control the size and shape of catalytic ensembles on the surface in order to promote specific reactions in many processes.<sup>145,146</sup>

## 6. Distribution of Adsorbates on the Surface

Finally, a more subtle effect associated with surface coverage is the fact that average surface concentrations do not necessarily reflect the local distribution of the species around the ensemble where the catalytic reactions occur. Because adsorbates often interact strongly with one another,<sup>7,147,148</sup> they may spread inhomogeneously across the surface, in a way that may depend on the history of the adsorption process. This is important in the context of catalysis because neighboring adsorbates modify the energetics of surface reaction in ways not explained by macroscopic kinetic models.<sup>149,150</sup> The free energy barriers associated with transition state theory can be expanded to include coverage-dependent terms, but that does not account for local fluctuations such as those related to the formation of surface islands. An example of the importance of islanding in catalysis is given by the results from our studies on the oxidation of carbon monoxide on Pt(111) single-crystal surfaces.<sup>151,152</sup> At least two kinetically distinct types of oxygen atoms were identified in that system, even though all the O adsorbates on that surface sit in identical sites at the start of the reaction. One possible explanation for such observation is that nearby oxygen atoms weaken the adsorption energy of CO, thus enhancing its reactivity. In fact, it was determined that when the oxygen is adsorbed in islands on the Pt(111) surface, the CO oxidation rate is up to 4 times faster than when the same number of oxygen surface atoms are randomly distributed on the metal surface.<sup>151</sup>

## NO Catalytic Reduction by CO on Rhodium Surfaces



**Figure 10.** Schematic depiction of the kinetic model proposed to explain the results from molecular beam studies on the reduction of nitrogen oxide by CO on Rh(111) surfaces.<sup>157,160,161</sup> Two key features are worth highlighting from this model, namely: (1) the formation of nitrogen islands; and (2) the preferential reaction of the edge N atoms with incoming NO molecules to form N<sub>2</sub> via a N–NO surface intermediate. This case exemplifies how the inhomogeneous distribution of adsorbates on the surface can modify the reactivity and selectivity of the overall system.

More recently, our investigations on the reduction of nitrogen oxide have revealed similar complications due to surface islanding.<sup>153–163</sup> It was found that the NO + CO/Rh(111) system, an interesting model for the study of the catalytic converters used in automobile exhausts, displays two kinetically different adsorbed nitrogen atoms.<sup>155</sup> On one hand, there is a buildup of a critical coverage of N atoms on the rhodium substrate before steady state is reached,<sup>156</sup> which then remains constant during the catalytic reduction of NO by CO.<sup>155</sup> In contrast, a small amount of additional N<sub>2</sub> desorption is detected immediately following any disturbance of the steady state condition. Molecular beam data indicate that it is the latter “weakly bonded” nitrogen that is associated with the steady-state reaction rates.<sup>154</sup>

Isotope labeling experiments have proven that the two types of nitrogen atoms are in fact the same surface species but in different local environments.<sup>155</sup> Specifically, it was shown that the “strongly bonded” nitrogen atoms (the first type) can be eventually removed from the surface during the steady-state conversion of NO with CO.<sup>155</sup> The kinetic results from isotopic switching experiments were reproduced quantitatively by a model involving the preferential recombination of atoms at the periphery of atomic nitrogen surface islands (Figure 10).<sup>161,163</sup> Based on this, it was suggested that the efficient production of molecular nitrogen, the rate-limiting step in these NO catalytic reduction processes, requires large ensembles of metal atoms to accommodate the formation of surface nitrogen islands. If that is the case, the structure of the metal particles in supported catalysts could play an important role in the performance of the catalysts, and that could be used to optimize their performance. In fact, it is already known that large particles are usually more efficient at promoting NO conversion than smaller ones, at least in the case of palladium-based catalysts.<sup>164</sup>

The formation of islands of adsorbates is also of great significance for the mechanism of the catalytic reduction of nitrogen oxide. In this context, it was found that the removal of the <sup>14</sup>N surface atoms initially deposited by <sup>14</sup>NO + CO mixtures after isotopic switching to an identical mixture with the <sup>15</sup>NO isotopologue occurs exclusively via the formation of

<sup>14</sup>N<sup>15</sup>N; no appreciable <sup>14</sup>N<sup>14</sup>N is made at any stage of the reaction with <sup>15</sup>NO.<sup>157</sup> The implication is that molecular nitrogen is produced not by recombination of two surface nitrogen atoms, as commonly believed, but via the formation of an N–NO intermediate at the edges of the nitrogen islands (Figure 10).<sup>157,159,160</sup> The decomposition of N<sub>2</sub>O on rhodium surfaces is indeed much faster than any of the other steps involved in the catalysis of NO reduction.<sup>165</sup> Perhaps the key in replacing rhodium with a cheaper material in catalytic converters is to find a metal that facilitates the dissociation of the undesirable N<sub>2</sub>O intermediate product before its molecular desorption.

## 7. Some Ideas for the Future

Our discussion above has highlighted some of the kinetic issues raised in recent years in connection with the surface chemistry of catalysis. It has long been recognized that kinetics lies at the heart of any catalytic process, but it has only been with the advancement of modern surface-sensitive techniques that the specific aspects of surface reaction kinetics have been tackled. Great progress has been made toward the understanding of the microscopic forces governing catalysis, but much more work is still needed in order to be able to design catalytic systems from first principles.

The gradual evolution of the symbiosis between basic surface-science studies and the design of catalytic processes of industrial interest has often led to an underestimation of the importance of the former to the advancement of the latter. When taking a historic perspective, however, the contributions of surface science to catalysis become evident. In particular, the characterization of chemical bonds between solid surfaces and adsorbates has helped develop a clearer definition of the catalytic problems. As mentioned throughout this Feature Article, kinetic and energetic measurements in model systems have advanced our ideas on how to improve selectivities toward specific reactions. A better understanding of the structure and electronic properties of solid surfaces has focused the search for catalytic materials as well as the design of specific catalytic sites. Even the optimization of the operational conditions of catalytic processes can now be viewed in terms of changes in the adsorption characteristics of the reactants.

As pointed out in the Introduction, we believe that the key issue for the future in catalysis is selectivity. The designing of selective catalysts is a particularly difficult task because of the sweeping changes in selectivity caused by small variations in the relative entropies and/or energies of competing reactions. It is for this reason that the specific issues raised in this paper, some of which may appear esoteric at first glance, are critical to the performance of catalysts in many real applications. It should be pointed out that our focus in this review on the kinetic and mechanistic aspects of catalytic reactions on surfaces stems only from the emphasis given to those issues in our laboratory. This bias does not mean to imply that there are no other pressing basic questions associated with heterogeneous catalysis. In particular, there is a particular need to extend the knowledge acquired in basic surface-science studies carried out under vacuum to realistic catalytic systems, as already alluded to above. This so-called “pressure gap” has been addressed by a number of research groups with mixed success: the effect of the solvent in chiral catalysis and the involvement of  $\pi$  bonded species in the hydrogenation of unsaturated hydrocarbons are just a couple of examples where the pressure gap has proven central to the description of the catalytic systems.

The nature of the active phase in real catalysts, which typically consist of small particles supported on high surface



area oxides, also needs to be better understood. The difficulty there is that the size and shape of supported particles influence their chemistry in ways not easy to reproduce with single crystals, foils, or films, a problem often referred to as the "materials gap". A number of laboratories are already working in this area, but much more research will be needed before we get a handle on the electronic and structural issues associated with such transition from model to real catalysts. To improve the selectivity of complex catalytic reactions, solids with more elaborated catalytic sites will likely be required. This implies not only the fine-tuning of the electronic properties of the surface via alloying or incorporation of multiple-component covalent materials such as oxides, carbides, and nitrides but also the control of complex site geometries, perhaps attempting to mimic enzymatic catalysis.

Underlying the search for answers to the fundamental questions mentioned above, there is also a need for the development of new experimental techniques and methodology.<sup>99</sup> In that respect, the future looks quite bright. From the kinetics point of view, the use of molecular beams specifically designed for the study of catalytic reactions should close the pressure gap between the model systems used in vacuum studies and the more realistic catalytic processes under atmospheric pressures.<sup>166,167</sup> More powerful computers and new quantum mechanics and Monte Carlo methods will also provide a more detailed account of the electronic and structural factors associated with specific kinetic pathways.<sup>168–171</sup> In addition, the identification of specific reaction intermediates on the surface of catalysts will be enhanced by new spectroscopic capabilities. For instance, the mapping of individual atoms on surfaces, unthinkable a few decades ago, is already a reality.<sup>172,173</sup> Scanning probes are just starting to blossom, and will soon aid in the characterization of individual molecular bond-forming and bond-breaking steps and in the manipulation of individual atoms and molecules on surfaces.<sup>174,175</sup> Additional advances in the use of optical spectroscopies for the study of nonvacuum interfaces (for the characterization of solid–liquid boundaries in particular) will unravel a new world of surface chemistry.<sup>141,176</sup> Finally, the advent of new sample preparation methods such as nanolithography and colloidal, chemical, and physical depositions will empower the surface-science community with the tools to address the problems associated with the materials gap, allowing for the emulation of more complex and realistic surface systems.<sup>177–179</sup>

Questions about catalysis are not just academic. Catalysis is a mature field with extensive practical applications in today's society. Indeed, the catalysis of petroleum refining, chemical manufacturing, and emission control combined amounts to a business of about \$10 billion worldwide, which produces goods worth more than a hundred times that amount. Future improvement of those well-established processes is likely to be incremental. On the other hand, the continuous demand for new products will require additional novel and innovative processes. For one, many of the existing stoichiometric organic synthetic reactions currently used in industry could be substituted by cheaper and less polluting processes based on heterogeneous catalysis. The need for pollution abatement and prevention also imposes new demands on catalysis, and new processes are periodically advanced for the control of emission gases as well as for remediation processes such as the cleaning of underground waters. Alternative energy sources will require creative catalytic processes, among others clean and small reforming reactors and efficient fuel cells. New selective chemical sensors are in

continuous demand. The number of problems where catalysis can have a big impact is constantly growing.

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