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# Mechanistic requirements for catalytic active sites

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## Abstract

The role of chemical kinetics in defining the requirements for the manufacturing of heterogeneous catalysts is discussed. A personal view is presented in which specific examples from our laboratory are provided to illustrate the role of the chemical composition, structure and electronic properties of catalytic active sites in determining reaction activity and selectivity. Manipulation of catalytic behaviour via the tuning of reaction conditions is also introduced.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

With the recent advent of nanotechnology, a variety of new tools have become available for the manufacturing of novel nanosize materials with unique structures and properties [1]. These advances offer particular promise for heterogeneous catalysis. To maximize its surface-to-volume ratio, the typical catalyst consists of an active phase dispersed as small nanoparticles on a high surface area support [2]. A number of conventional techniques are available for the preparation of such catalysts, including impregnation, incipient wetness, coprecipitation, and sol–gel methods [3–5]. However, those all suffer from the same main limitation, namely, they produce complex solids with wide distributions of particle sizes and shapes which depend in a non-easy-to-predict way on the details of the preparation procedures. Catalyst preparation is still considered an art.

New methodology is needed to synthesize supported heterogeneous catalysts in a controlled manner. Several fresh ideas have recently been introduced for this purpose. New chemical approaches include the use of colloidal particles [6, 7], carbonyls [8], and other organometallic clusters [9] as precursors for the supported catalytic particles. Physical methods such as vapour deposition [10] and electron beam lithography [11] have also been attempted. However, the impact of these new directions to the practical manufacturing of catalysts for industrial use is still far from being realized.

As our ability to design and prepare specific nanostructures improves, it is important to keep in mind what the ultimate goals are as far as the optimization of catalytic processes is concerned. It has long been recognized that the performance of many catalytic processes depends strongly on the nature of the catalyst [2]. One of the most traditional and widely accepted manifestations of this correlation is the so-called structure sensitivity seen for reactions whose activity or selectivity depend on the average particle size of the catalyst [12]. This dependence has been ascribed to a combination of structural and electronic properties, both of which change appreciably with particle size in the nanometre range.

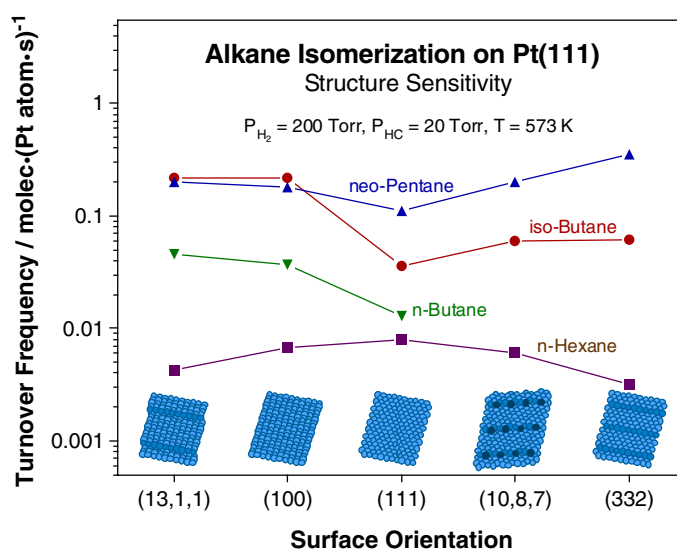
The requirements for a catalytic reaction can be described in terms of the specific arrangement of the surface atoms responsible for the promotion of the surface reaction steps involved. This arrangement is often referred to as the catalytic active site, and can be defined by a particular local ensemble of atoms within the exposed solid surface. The identification of such sites is the first step in developing catalyst designs from first principles. A discussion of the requirements imposed on such catalytic active sites by the mechanisms of the catalytic reactions is the subject of this paper. Ours does not intend to be a comprehensive review on this subject, but rather a critical and personal view based on some results from studies in our laboratory. Our central message is that a good understanding of the chemical process to be catalyzed helps focus the design of better catalysts.

## 2. Background

Heterogeneous catalysis is quite a mature field, and the effect that the structure of the solid catalyst exerts on its performance has been recognized for several decades [13]. This, however, is not a general phenomenon. Some catalytic processes, hydrogenations and dehydrogenations in particular, often require mild conditions, and appear not to depend strongly on the specific characteristics of the catalyst but only on the overall chemical composition of the active phase. In fact, most metal catalysts used for hydrocarbon conversions become covered with a layer of carbonaceous deposits which masks the specific structural details of the surface [14, 15]. On the other hand, other reactions are more demanding, requiring higher pressures and temperatures, and are likely to involve the bare surface of the catalytic material instead [16]. In those cases, the structure of the catalytic surface does matter, because the key reaction steps typically involve specific multi-atom surface ensembles. When both structure sensitive and structure insensitive reactions are possible, the designing of preparation methodologies for the creation of specific active sites can be a powerful tool to develop catalysts with good selectivities toward the desired products [17].

Traditional studies on structure sensitivity in catalysis have relied primarily on indirect observations, namely, on the changes in activity and/or selectivity often detected as a function of variations in size and/or shape of the supported catalytic particles [18]. With the advent of modern surface characterization techniques, however, a more direct definition of the active sites has become possible [19, 20]. Initial studies in this direction have relied on kinetic measurements of catalytic processes using model single crystals with specific exposed surface planes [21, 22]. A striking example of the success of this approach is provided by the case of ammonia synthesis on iron surfaces, for which the (111) surface was shown to be several orders of magnitude more active for both nitrogen activation [23] and ammonia production [24] than the (110) plane. This is explained by the particular catalytic activity of iron atoms with seven coordinated iron neighbours [25].

Figure 1 displays a different example of catalytic structure sensitivity on single crystal surfaces, that of the conversion of alkanes on platinum [26, 27]. The catalytic activities measured for the isomerization of *n*-butane, *iso*-butane, *neo*-pentane and *n*-hexane are



**Figure 1.** The dependence of the isomerization activity of several alkanes on the structure of the platinum single-crystal surface used as catalyst [26]. These results indicate a direct correlation between catalytic activity and the nature of the surface atomic ensemble, and help to better understand the requirements for the catalytic active site. Notice, for instance, the significantly larger activity of (100) planes for *n*-butane and *isobutane* conversion, and the changes in reaction rates as steps and kinks are introduced on the surface. Better selectivities in hydrocarbon conversion processes such as reforming may be accomplished by preparing catalysts with a maximum of (111) microfacets exposed.

displayed for a number of surface planes, including the thermodynamically stable (111) and (100) flat faces, the (332) and (13, 1, 1) planes, which contain (111) and (100) terraces 6–8 atoms wide followed by monatomic steps, and the (10, 8, 7) surface, with its high density of low-coordination kink platinum atoms. Several conclusions were drawn from these studies:

- (1) the isomerization of light alkanes is maximized by (100) microfacets;
- (2) maximum rates for competing hydrogenolysis reactions are seen on Pt surfaces with high concentrations of steps and kinks;
- (3) by contrast, none of the isomerization, cyclization, or hydrogenolysis reactions displays any noticeable dependence on surface structure with *n*-hexane; and
- (4) the distribution of hydrogenolysis products varies with terrace structure.

### 3. Island formation

Even seemingly simple reactions may impose stringent requirements on the structure of the catalytic surface. One reason for this stems from the fact that surface reactions, even elementary steps, can display a complex kinetics because of the strong interactions among neighbouring adsorbates [28]. For instance, molecular beam experiments carried out in our laboratory have indicated that kinetically distinct types of oxygen atoms are identifiable on Pt(111) surfaces during the isothermal oxidation of CO, even though they all sit in identical sites at the start of the reaction [29]. In fact, it was shown that different kinetics may be obtained on surfaces with the same nominal concentrations of reactants depending on the preparation procedure [30]. These observations are explained by a lowering of the reaction activation barrier with oxygen

islanding: the carbon monoxide that adsorbs in the middle of such oxygen islands is more reactive than that bonded on clean platinum patches because of the repulsive interactions between the two species.

Another example of the key role played by the formation of adsorbate islands on the surface of the catalysts is that of the reduction of nitrogen monoxide on rhodium [31–33]. Molecular beam investigations again pointed to two types of kinetically different nitrogen atoms on the surface. In this case, however, there is an initial build up of a critical coverage of atomic nitrogen before the start of the production of  $N_2$ . In addition, a small amount of another type of nitrogen-containing intermediate appears to be present on the surface during catalysis but to desorb rapidly after the removal of the gas-phase reactants. It is the concentration of this second species that correlates with the kinetics of NO reduction.

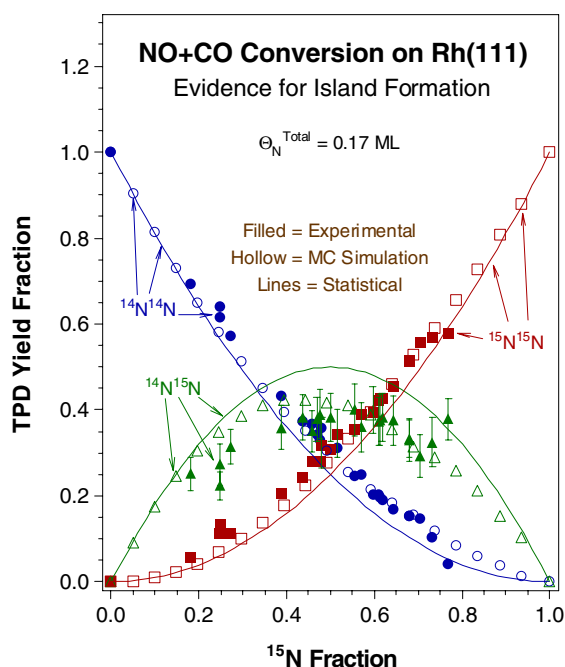
Further isotope switching experiments indicated that the two types of kinetically different nitrogens are not likely to represent different adsorption sites, but rather similar adsorption states with adsorption energetics modified by their immediate surrounding environment on the surface [34]. In one set of isotope labelling studies, a Rh(111) single-crystal surface was exposed sequentially to  $^{14}NO + CO$  and  $^{15}NO + CO$  gas mixtures for varying times and then probed by temperature-programmed desorption (TPD) to determine the nature of the layer of adsorbed atomic nitrogen present on the surface during catalysis [35, 36]. The results, summarized in figure 2, indicate a non-statistical distribution of isotopes in the molecular nitrogen produced, the yield of the mixed  $^{14}N^{15}N$  isotopomer being significantly lower than that expected on statistical grounds. Monte Carlo simulations explained the observed isotopic distributions in terms of the formation of islands with the nitrogen isotopes distributed in a layered structure, the  $^{14}N$  atoms in a core surrounded by a  $^{15}N$  outer shell.

A second set of experiments was designed to directly measure the rates of all isotopically-labelled molecular nitrogen produced during the isothermal steady-state reduction of NO to  $N_2$  by CO on the Rh(111) surfaces [37, 38]. Surprisingly, the replacement of surface  $^{14}N$  by  $^{15}N$  upon switching the isotopic nitrogen label in the NO (from  $^{14}NO$  to  $^{15}NO$ ) was determined to occur via the exclusive formation of  $^{14}N^{15}N$ . This result provides direct kinetic evidence for a mechanism for molecular nitrogen production involving the formation of an N–NO intermediate. The key observation in connection with the argument put forward in this report is that such intermediate appears to form preferentially at the periphery of large atomic nitrogen islands (figure 3). This suggests that the structure sensitivity reported for some NO reduction catalysts [39] may be due to the need for large (111) terraces to accommodate the nitrogen surface clusters. This is a hypothesis we are presently testing in our laboratory.

#### 4. Chemical composition of active sites

In more complex reactions, the demands on the catalytic site may involve a combination of surface species in close proximity on the surface. This certainly appears to be the case for the partial oxidation of hydrocarbons [40]. The balance between dehydrogenation and dehydration in organic alcohols provides a classical example of the central role that chemical kinetics plays in controlling selectivity in catalysis: while acidic oxides such as  $\gamma$ -alumina often promote alcohol dehydration, basic oxides such as magnesia and calcium oxide typically favour alcohol dehydrogenation instead [41, 42]. The oxidation of alkanes is also closely connected to that of alcohols, because they both may involve the same initial alkoxide intermediates [40, 43]. Kinetic control in these systems requires the design of catalysts with chemically optimized active sites.

We have been investigating mechanistic issues related to this hydrocarbon oxidation catalysis by using nickel oxide model surfaces. In our work, nickel single-crystal surfaces

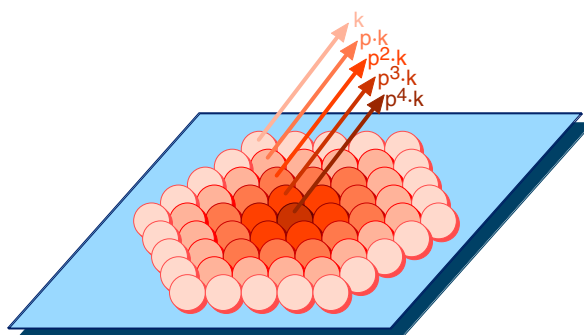


**Figure 2.**  $^{14}\text{N}^{14}\text{N}$ ,  $^{14}\text{N}^{15}\text{N}$ , and  $^{15}\text{N}^{15}\text{N}$  TPD yield fractions as a function of the isotopic composition of the atomic nitrogen present on the surface during the steady-state reduction of NO by CO on a Rh(111) surface [35]. The filled symbols correspond to the data obtained experimentally by integration of temperature programmed desorption (TPD) traces after sequential molecular beam kinetic runs using  $^{14}\text{NO} + \text{CO}$  and  $^{15}\text{NO} + \text{CO}$  mixtures. The solid curves correspond to the yields expected on statistical grounds, while the open symbols correspond to the results from a Monte Carlo simulation that assumes the formation of surface islands. The clear deviations from statistical predictions seen in the experimental data attest to the non-homogeneous distribution of the adsorbates.

are oxidized and characterized *in situ* under ultrahigh vacuum by both physical and chemical means [44, 45]. Novel ways of enhancing the growth of such oxide films were found [46], and defective oxide sites were emulated by purposely damaging crystalline NiO films [47]. Hydroxide surface species were added by appropriate treatments with water vapour [48, 49]. All these techniques provided a versatile set of tools for the preparation of a variety of specific surface sites.

The properties of the active sites created on the model nickel oxide surfaces prepared by the methods mentioned above were then fully characterized using a combination of surface sensitive techniques. The most detailed information about specific chemical sites was obtained by using a chemical approach. Carbon monoxide in particular was proven to be an excellent local probe for the determination of the oxygen coordination and oxidation state of individual nickel surface atoms [47]. As an example of how that worked, the data in figure 4 highlight the observed changes in desorption temperature, that is, adsorption energy, associated with the different sites produced by controlled oxygen treatments of Ni(110) surfaces. Significant and discrete changes in adsorption energy, from 10 to 30 kcal mol<sup>-1</sup>, were seen as a function of the number of oxygens coordinated to a specific nickel atom. Although the chemistry of ammonia on those surfaces was found to be quite a bit more complex, it was also shown to be helpful for probing the lability of hydrogens in OH surface groups via H-D exchange reactions [50, 51].

### Island Model for the Conversion of NO+CO Mixtures on Rh(111)



**Figure 3.** Schematic depiction of the model used to explain the kinetics of reduction of NO by CO on rhodium surfaces [36]. Surface nitrogen atoms are proposed to aggregate in islands approximately nine atoms in diameter, and to react according to the distance from the perimeter of the island. While the outermost N atoms are consumed at the steady-state rate of conversion of NO, those in each subsequent layer are removed at a rate  $p$  times slower than that from the next outer shell. This dependence is justified by the formation of N–NO surface intermediates between the peripheral nitrogens and new NO incoming reactants. Surface islands such as this require large flat terraces, a fact that may explain the surface sensitivity of the NO reduction catalytic processes.

Oxygen atoms at the end of –Ni–O– surface rows were found to be particularly active towards oxidation reactions with other adsorbates.

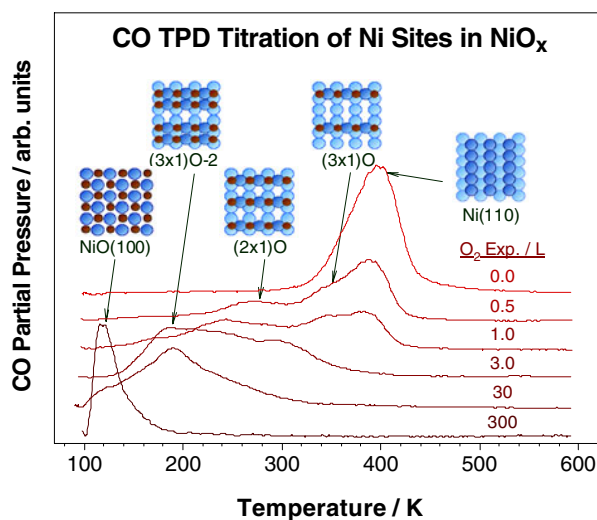
Separate studies of the activity of oxide model surfaces towards the conversion of hydrocarbons have highlighted the importance of well-defined surface ensembles of complex stoichiometry for the promotion of specific reactions. In terms of the partial oxidation of alkyl surface groups, the presumed intermediates formed after alkane activation, it was shown that selectivity towards the production of aldehydes or ketones is only possible on partially oxidized nickel surfaces [52, 53]. Several concrete criteria were identified in these studies:

- (1) the initial alkyl intermediates adsorb on nickel, not oxygen, sites [44];
- (2) oxygen insertion into the nickel alkyl bond is facile, but requires near proximity of the oxygen and alkyl adsorbed species [54];
- (3) the resulting alkoxide surface species is the same intermediate involved in the oxidation of alcohols [55];
- (4) at higher temperatures, alkoxides undergo preferential  $\beta$ -hydride elimination to ketones or aldehydes; and
- (5) surface hydroxide groups promote this partial oxidation pathway.

All these ideas are summarized by the model schematically shown in figure 5. It can be seen there that partial oxidation catalysis may require a complex ensemble of metal, oxygen, and hydrogen atoms.

## 5. Adsorption geometries and catalyst modifiers

Clearly, the structural and electronic details of the surface site are crucial in defining catalytic activity. Other parameters (reaction conditions in particular) may play a key role for this as well. Indeed, reaction temperatures and reactant pressures often determine the activity



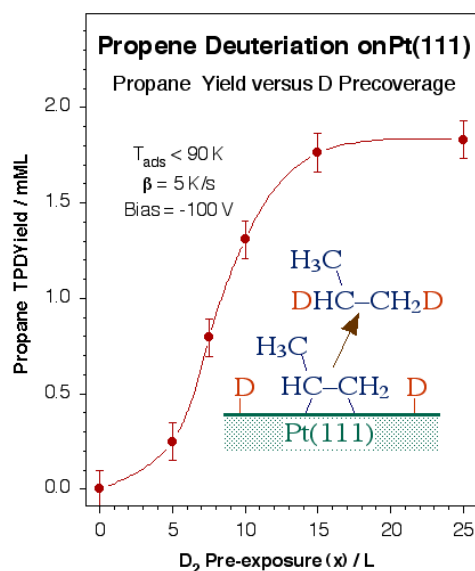
**Figure 4.** CO titration of local adsorption sites on a Ni(110) single-crystal surface exposed to different amounts of oxygen gas [47]. The various peaks in the CO TPD traces shown here are indicative of different adsorption strengths, going from approximately  $30 \text{ kcal mol}^{-1}$  on clean nickel (the 400 K peak) to less than  $10 \text{ kcal mol}^{-1}$  in the case of NiO (the feature about 120 K). Based on the known structures for this O–Ni(110) system, the five adsorption states detected in these experiments can be directly associated with different coordination numbers of oxygen atoms around the nickel adsorption sites. The reverse behaviour was observed during ion sputtering of NiO crystalline films, suggesting that our O–Ni(110) surfaces may be reasonable models for more realistic defective nickel oxide catalysts. The establishment of correlations between the formation of different O–Ni sites and the selective reactivity toward specific reactions can aid in the design of better catalysts.



**Figure 5.** A schematic representation of the proposed catalytic site required for the partial oxidation of alkanes and alcohols. In this model, the oxygen atoms at the end of –Ni–O– rows are responsible for hydrocarbon conversion, interacting via hydrogen-bonding with the reactant alkyl species bonded to adjacent nickel atoms. Nearby hydroxide surface species are also required to enhance the oxygen insertion that leads to alkoxide formation, the first step in the oxidation process. The use of defective oxides with large numbers of partially oxidized nickel atoms, electronically unsaturated oxygen atoms, and neighbouring OH groups, all appear to be required for the selective oxidation of alkanes or alcohols towards aldehyde or ketone production.

and, perhaps more importantly, selectivity of many industrial catalytic processes. From a microscopic point of view, reaction conditions affect both the adsorption of the reactants and their subsequent surface activity. It is quite intuitive to think that the reactivity of a specific bond in a chemisorbed species may depend on its degree of interaction with the surface,



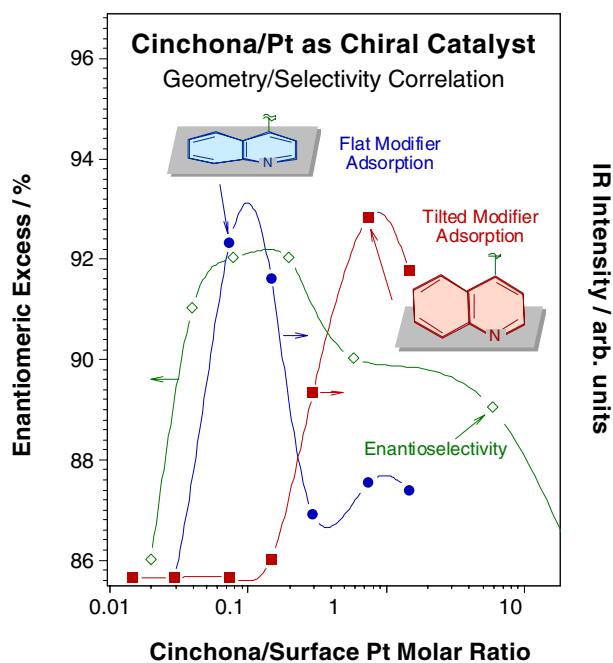


**Figure 6.** Total propane TPD yield from deuteration of 1.5 L of propylene on Pt(111) as a function of deuterium pre-dose [71]. The propane product distribution in terms of the number of deuterium atoms incorporated per propylene molecule does not change significantly with deuterium coverage (data not shown), but the total yield increases in a nonlinear fashion. This deviation from simple kinetic behaviour is ascribed to changes in reactivity due to variations in adsorption geometry.

something likely to be determined by the degree of proximity between the reacting moieties and the substrate [20]. For instance, in the case of carbon monoxide activation in processes such as methanation and Fischer Tropsch, it is known that the typical initial adsorption of the reactant is with the C–O bond perpendicular to the surface [56]. Interestingly, though, a tilted geometry has been reported on Cr(110) [57], Fe(100) [58] and Mo(100) [59, 60] having both a low C–O stretching frequency and an unusually long C–O bond. This suggests a particular geometry for the precursor to dissociation.

A straightforward link can be established between the partial pressure of a given reactant and its coverage on the surface of the catalyst. A somewhat less clear but quite revealing connection can also be identified between that coverage and the geometry adopted by the adsorbate on the surface [61, 62]. This correlation can be understood in terms of the strong intermolecular interactions associated with high-density systems such as those encountered in adsorbates on solid surfaces, as mentioned above [17, 28]. Changes in adsorption geometry with surface coverage are indeed common with adsorbed hydrocarbons, and have been well documented for many aromatic rings [63, 64] as well as for alkyl [61, 63, 65] and alkoxide [66] surface moieties. Adsorption geometries may also be affected by the structure of the surface, as in the case of ethylene on copper, where the typical flat geometry observed on Cu(111) [67] and Cu(100) [68] is not available on Cu(110) [69, 70].

In contrast with the structure of the surface active sites, adsorbate geometries during catalysis are difficult to control. Nevertheless, it has been possible in some instances to directly correlate changes in coverages and/or adsorption geometries with variations in reactivity and/or selectivity. Figure 6 provides an example where the pre-dosing of deuterium was used to enhance hydrogenation pathways at the expense of dehydrogenation reactions in propene adsorbed on Pt(111) [71]. The relevance of these data to the present discussion comes



**Figure 7.** *In situ* infrared spectroscopy data pointing to the correlation between adsorption geometry and catalytic selectivity in the case of the enantioselective hydrogenation of ethyl pyruvate by cinchonidine-modified platinum [82]. Three distinct adsorption regimes were identified for the modifier depending on its concentration in the liquid solution, namely, no discernible uptake below 5% of saturation, flat-lying surface bonding between 5% and 20%, and a tilted configuration above 20%. A revealing connection was identified with previous reports of optimum activity and enantioselectivity with the intermediate concentrations of the chiral modifier associated here with the flat adsorption of the aromatic ring.

from the observation that the propane yield in those experiments does not increase linearly with deuterium surface concentration, as expected using traditional kinetics models [28], but rather abruptly after reaching a critical minimum coverage. This behaviour can be traced back to changes in the adsorption for the reacting propene [72]. Sudden variations in selectivities between hydrogenation and dehydrogenation steps with hydrocarbons are in fact quite common [15, 73–79], and are seen under catalytic conditions even if the ratio of the reactants in the reaction mixture is maintained constant. One classic surface-science example of this is that of the conversion of cyclohexene on Pt(111), where extensive dehydrogenation to benzene is seen at pressures below  $10^{-4}$  Torr but a predominance of hydrogenation to cyclohexane occurs above 1 Torr [80].

A particularly exciting possibility in terms of defining catalytic selectivities via the control of adsorption geometries has been recently advanced for the bestowing of enantioselectivity to regular hydrogenation catalysts by using a chiral modifier [81]. Figure 7 illustrates this point for the case of the hydrogenation of  $\alpha$ -ketoesters with cinchonidine-modified platinum surfaces [82, 83]. Our *in situ* infrared characterization of the adsorption at the liquid–solid interface where the reaction occurs have proven that the performance of the cinchonidine/platinum system is optimized by a flat-lying adsorption geometry of the aromatic ring of the cinchona modifier, and that that geometry depends strongly on the concentration of the modifier in the solution [82, 84, 85]. Additional improvements in performance can also be

induced by changes in solvent, dissolved gases, temperature, and other reaction parameters, all of which appear to exert a direct influence on the adsorption of the chiral modifier on the surface [86, 87].

The interpretation of the changes in activity and selectivity often observed in hydrocarbon conversions is complicated further by the build up of strongly bonded carbon-containing residues on the catalysts used [14, 21]. Perhaps the most important role of these carbonaceous deposits to the catalytic cycle is as tempering agents for the high activity of the clean metal [88, 89]. This is particularly clear with unsaturated hydrocarbons, for which a new  $\pi$  bonding state [72, 90, 91] makes catalytic hydrogenation processes possible [92, 93]. More demanding reactions such as reforming and hydrogenolysis, on the other hand, are likely to still require exposed metal atoms instead [94, 95]. To improve the performance of a given hydrocarbon conversion catalysts, therefore, the build up of the carbonaceous deposits needs to be fine-tuned. This is typically achieved by addition of a second metal [96, 97] and/or other additives such as sulfur, alkaline metals, and chlorine [98, 99]. In fact, both alloying and additives are used extensively to control the size and shape of catalytic ensembles on the surface in order to promote specific reactions [100, 101]. Here is another example of how the reaction mechanism defines the requirements for the active catalytic site.

## 6. Concluding remarks

To conclude, it is worth reiterating the main thesis of this report, that the requirements for the surface active sites in heterogeneous catalysis are defined by the mechanistic details of the reactions involved. Examples were provided above for cases where those active sites may require complex stoichiometries or chemical compositions. Instances were also mentioned in which the main criteria for optimizing activity and/or selectivity are the size and geometrical arrangement of the ensemble of surface atoms required for the promotion of the desired reactions. Electronic properties are to be given similar considerations when designing catalysts. Finally, the performance of the catalyst can in some cases be defined by tuning the reaction conditions.

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