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Surface chemistry of hydrocarbon fragments on transition metals: towards understanding catalytic processes*

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The central issue of this review is the importance of selectivity in heterogeneous catalysis. The implications of our mechanistic studies on model systems to the interpretation of catalytic processes are discussed. In particular, it is our thesis that the optimization of catalytic selectivity may require a different approach than that needed to increase overall catalytic activity. This is so because a given intermediate in the reaction mechanism may be slow to form, but able to react by following more than one relatively fast pathway. In the case of hydrocarbon reforming, while activity is often controlled by alkane activation, selectivity is likely to depend on the regioselectivity of the subsequent dehydrogenation of the resulting alkyl surface intermediates. Similar arguments can be used to explain the selectivity between dehydrogenation and dehydration reactions on alcohols. Additional complications arise from the build up of carbonaceous deposits on the surface of the catalyst under reaction conditions. Surface-science studies have led to the conclusion that these deposits modify the properties of the exposed catalytic metal, opening up new channels for mild reactions but still allowing for the occurrence of the more demanding reactions involved in hydrocarbon reforming and oxidation processes. Lastly, catalyst modification can be introduced in a controlled fashion, as in the case of the bestowing of chirality to normal hydrogenation catalysts by the addition of small amounts of chiral cocatalysts to the reaction mixture. A brief survey of our recent investigation of these systems is provided.

KEY WORDS: selectivity; heterogeneous catalysis; surface chemistry; transition metals.

1. Introduction

Selectivity is arguably the most important issue to be addressed in order to usher catalysis into the twenty-first century [1–3]. Clearly, selective catalysis brings several important advantages to industrial processes by consuming less reactants, bypassing subsequent separation steps, and avoiding the need for the disposal of potentially polluting by-products. Unfortunately, the increasing demands of the industrial processes required to manufacture new sophisticated chemicals for pharmaceutical, agricultural, materials, and environmental applications, among others, often involve complex reaction networks difficult to control. Nowadays, optimizing the selectivity of a given process is often more important than increasing the overall reaction rate.

Chemical selectivity in catalytic processes, and in fact catalysis itself, is most often defined by the kinetics of the reactions involved [4, 5]. This is so because the thermodynamically favored products expected from most reaction mixtures are often of little commercial value. The problem is particularly acute in the case of processes involving hydrocarbons. For instance, complete hydrocarbon oxidation leads to the formation of carbon dioxide and water, products of low industrial value; partial oxidation to oxygenates such as alcohols, aldehydes, ketones, and organic acids requires kinetic control [6, 7]. Similar arguments can be made for hydrocarbon reforming [8, 9], and also for the synthesis of most organics and other fine chemicals [10, 11].

A brief survey of the literature indicates that the desire to improve selectivity in catalytic processes is already widely acknowledged. The difficulty arises when selectivity is to be achieved at the expense of overall reactivity. This may come about because the steps in a reaction mechanism that define selectivity are not necessarily the same as those that control the reaction rate. This point is illustrated by the energy diagram for a hypothetical three-step mechanism shown in figure 1. There, a high barrier for the conversion of the reactant to the intermediate limits the turnover frequency of the overall process. Therefore, to accelerate that process, the catalyst has to be tuned to facilitate the first reaction step, that is, to lower $\Delta G^{\ddagger}_{\mathrm{rls}}$. On the other hand, if selectivity toward the formation of Product 1 versus Product 2 is what matters most, the parameter to improve is the difference in activation barriers from the intermediate to each of those products, $\Delta G^{\ddagger}_{1} - \Delta G^{\ddagger}_{2}$. The criteria for lowering $\Delta G^{\ddagger}_{1}$ with respect to $\Delta G^{\ddagger}_{2}$ are not likely to be the same as required to modify $\Delta G^{\ddagger}_{\mathrm{rls}}$.

We in our laboratory have been studying a number of reaction mechanisms on model systems in order to address the kinetic issues highlighted above. Our approach has been to isolate key surface intermediates and to study their elementary reactions by using a

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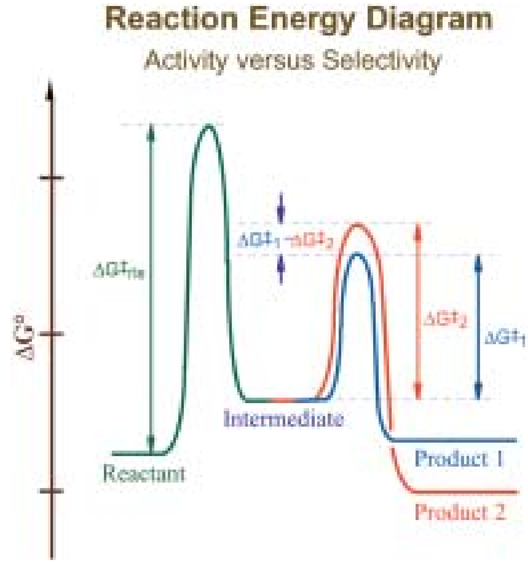

Figure 1. Schematic energy diagram of a hypothetical catalytic process illustrating the different criteria needed to optimize total reactivity versus selectivity. In this example, the overall rate is controlled by an initial conversion of the reactant to the intermediate, and can be improved by lowering the energy barrier of that reaction, $\Delta G^{\ddagger}_{\mathrm{rls}}$. On the other hand, selectivity, defined as the yield ratio of Product 1 over Product 2, is determined by the difference in barrier heights for the two reactions available to the intermediate, $\Delta G^{\ddagger}_1 - \Delta G^{\ddagger}_2$. Tuning selectivity is a subtle task, since a relative variation of about 10% in the absolute value of either $\Delta G^{\ddagger}_1$ or $\Delta G^{\ddagger}_2$ is sufficient to switch from the exclusive formation of one product to the other [3]. We believe that being able to control selectivity is the main issue facing catalysis in the future.

combination of modern surface-sensitive techniques [12, 13]. In this review, we present a few examples of the type of information that we have been able to extract from such studies. Our focus is on hydrocarbon conversion, in particular, on dehydrogenation steps. It is argued that the regioselectivity of early dehydrogenation steps may not control overall reactivity, but often define selectivity in processes such as hydrocarbon reforming and partial oxidation. A discussion is also provided on the relevance of surface-science studies to reactions occurring under catalytic conditions. Finally, the idea of modifying catalytic surfaces to improve selectivity in chiral processes is briefly introduced.

2. Hydrocarbon reforming

Hydrocarbon reforming, as used in oil refining, provides an excellent example of the need to design selective catalysts to favor specific pathways within a complex reaction network. In those processes, the original distillate during gasoline reforming, mainly a mixture of straight chain alkanes, is converted to branched and cyclic compounds while avoiding hydrogenolysis to lighter hydrocarbons [14, 15]. It is widely accepted that the rate-limiting step in these processes is the initial dissociative adsorption of the alkanes, which requires the activation of a C–H bond and presumably leads to the formation of the corresponding chemisorbed alkyl intermediates [16, 17]. Here, we advance the notion that selectivity in reforming is defined by the location of the first hydrogen abstracted from those surface alkyl species [3, 8, 18]. The basis for this assertion is briefly discussed below.

In order to study the chemistry of alkyl species on surfaces, we first need to turn our attention to the development of procedures for the isolation of these moieties cleanly on metal surfaces. Since the direct activation of alkanes to surface alkyls is typically the rate-limiting step in hydrocarbon conversion, that step is often difficult to emulate directly under the vacuum conditions used in most modern surface-science studies and also difficult to stop at the production of the alkyl moieties. A number of somewhat successful methods have been advanced over the last decade for the surface preparation of alkyl surface species under controlled conditions, including the deposition of gas-phase radicals made by pyrolysis of appropriate precursors [19], the soft landing of gas-phase cations [20], and the thermal or photolytic activation of adsorbed alkanes [21–23]. We, in our laboratory, have developed a versatile approach based on the thermal activation of adsorbed alkyl halides [24–28], a method that can be extended to the preparation of many other hydrocarbon species such as carbenes [29–33], vinyls [34, 35], allyls [36–39], metallacycles [40–44], and oxametallacycles [45–47]. This methodology has since been adopted by several other research groups [48–51].

The reactivity of C–H bonds in adsorbed hydrocarbons is expected to depend on their position in the carbon chain, in particular, in reference to the distance from the surface. Activation of different carbon–hydrogen atoms leads to the formation of structurally different new intermediates. This is illustrated in figure 2 for the case of the *sec*-butyl species that result from isobutene activation at one of the terminal carbons. Following the nomenclature commonly used in organometallic chemistry [52, 53], the three types of hydrogens present in the *sec*-butyl intermediate can be labeled as α (the hydrogens on the carbon directly bonded to the surface), β (on the adjacent, central carbon), and γ (in the terminal, unactivated methyl groups). Elimination of one hydrogen atom from the α, β, or γ position results in the formation of an alkylidene, alkene, or metallacycle species, respectively (figure 2).

Our experiments on the thermal chemistry of alkyl species adsorbed on transition metal surfaces have clearly indicated that the preferred dehydrogenation step is via the removal of a hydrogen atom from the β-position [26, 49, 53, 54]. The earliest indication of the occurrence of this step came from temperature-programmed desorption studies using ethyl iodides regioselectively labeled with deuterium atoms [55], but more direct evidence is now available in the form of the

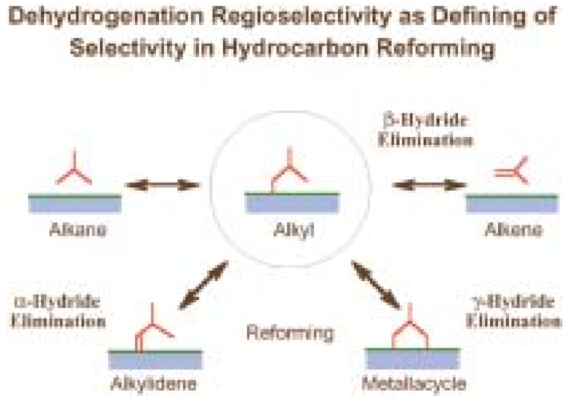

Figure 2. Simplified reaction mechanism for the catalytic reforming of hydrocarbons on transition metal surfaces. Isobutane is used here as a prototypical example of the alkanes that constitute the main components in crude oil. The rate-limiting step in these processes is the initial C–H bond activation that yields alkyl surface intermediates (*sec*-butyl in this case), but it is our contention that the selectivity of the overall process is defined by the regioselectivity of the subsequent dehydrogenation reactions. β-hydride elimination dominates the chemistry of adsorbed alkyl groups, but only leads to fast alkane–alkene equilibria; what determines selectivity between the desirable cyclization and isomerization reactions and the undesirable hydrogenolysis is the relative rates between the γ- and α-hydride elimination steps [8].

detection of the resulting olefin both adsorbed on the surface [56] and in the gas phase after desorption [24, 27]. A series of creative experiments by a number of research groups have also helped advance a fairly clear microscopic picture of the transition state of this dehydrogenation step. In particular, the anionic nature of the leaving hydrogen has been demonstrated by using fluorine substitution [57], and the planarity of the metal–carbon–carbon–hydrogen–metal four-atom cycle formed during the transfer of the hydrogen atom from the β-carbon to the metal has been tested using cyclic alkyl species with different ring strains [58]. A schematic representation of the transition state for this step, which, based on its similarity with the analogous organometallic reaction may be denoted as β-hydride elimination, is shown in figure 3.

β-hydride elimination explicitly accounts for the fast production of olefins during reforming (figure 2) that commonly leads to the establishment of rapid alkane-alkene equilibria [59, 60]. Together with C=C insertion into metal-hydrogen bonds and alkyl-hydrogen reductive elimination steps, it also explains H-D exchange and double-bond migration [29, 36, 39, 40, 56, 60–72]. More demanding reforming processes, on the other hand, require dehydrogenation steps at other positions in the hydrocarbon chain. Inspection of past studies on supported catalysts has led us to suggest that while hydrogen removal at the γ-carbon may be responsible for desirable isomerization and cyclization steps [73–75], dehydrogenation at the α-position is likely to end in the production of undesirable hydrogenolysis products instead [76].

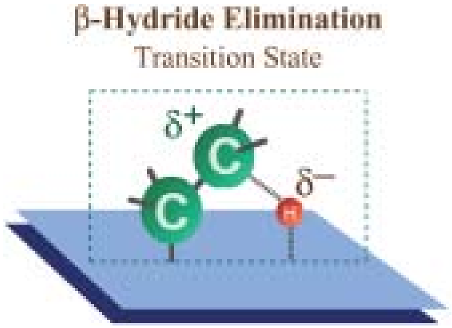

Figure 3. Transition state for β-hydride elimination of adsorbed alkyl groups. The prevalence of dehydrogenation at the β-position was initially demonstrated by TPD experiments with deuterium-labeled alkyl halides [54, 55]. The anionic nature of the leaving β-hydrogen was proven by the large change in dehydrogenation rate induced by substitution of the γ-hydrogens with more electronegative fluorine atoms [148]. The planar geometry of the four-center transition state was tested by using cyclic alkyls with different structural constraints [49]. The preference for hydride elimination from inner (more substituted) carbons was shown by the selective 2-hexene formation from 2-hexyl adsorbates [87]. All these observations parallel those reported for β-hydride eliminations in organometallic complexes [53].

Although hydride eliminations from the α- and γ-positions are clearly much less favorable than from the β-carbon, they can still be probed by using adsorbates with no β-hydrogens such as methyl, neopentyl, and benzyl moieties [77, 78]. Figure 4 summarizes the main temperature-programmed desorption data available in the literature on α-hydride elimination from methyl groups versus β-hydride elimination from ethyl surface species [24, 77, 79–86]. The values provided, which correspond to the temperature maxima, $T_{\max}$, for the desorption of the methane and ethylene produced by the

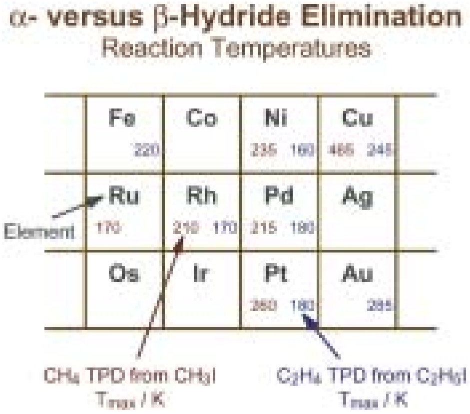

Figure 4. Comparison of α- versus β-hydride elimination reaction temperatures across the periodic table. The numbers in each cell correspond to the temperature maxima for the associated methane (left) and ethylene (right) production reactions during temperature-programmed desorption with methyl and ethyl surface species respectively [25, 49, 53]. In general, higher reactivities are seen for all reactions with early transition metals and shorter hydrocarbon chains. More significant are the variations in relative rates between α- and β-hydride eliminations: the former appears to be particularly difficult with coinage metals.

α- and β-hydride elimination steps respectively provides us with an indication of the degree of difficulty of the original dehydrogenation reactions. In spite of the scarcity and scatter of the data, some trends can already be identified. For one, it is clear that dehydrogenation reactions are easier with light and early transition metals, following similar trends than those seen for many other reactions. Also, on a given metal, α-hydride elimination is always more demanding than β-hydride elimination, as stated before. What is particularly important for our discussion here is the fact that the temperature difference between the two reactions varies significantly with the nature of the metal. Compare, for instance, the differences in $T_{\max}$ on platinum (260 versus 180 K) or nickel (235 versus 160 K) with those on copper (465 versus 245 K); it appears that α-hydride elimination is particularly difficult in coinage metals. In fact, those metals often favor alkyl coupling instead [48], hence the lack of hydride elimination data for them, for silver, in particular. Finally, in the few cases where work has been performed on different planes of the same metal, no significant structure sensitivity has been identified, although the data for this are still too scarce to draw meaningful conclusions [66, 87].

Temperature-programmed desorption experiments are usually carried out in irreversible vacuum conditions and typically lead to the observation of reactivity at temperatures much lower than those used in catalytic processes. Different types of experiments were therefore required to extrapolate the resulting kinetic information from work on model systems to catalytic reforming processes. In one case, the multiple H-D exchange seen in methyl groups on Pt(111) was used to estimate the activation barrier for α-dehydrogenation at a value of about 2 ± 1 kcal/mol higher than that for hydrogen removal from the β-position [29, 64, 66, 82, 88, 89]. Two additional experiments also allowed us to compare α- and β-hydride elimination rates directly on ethyl groups. The first, based on the relative rate of formation of different ethylidyne isotopologues from α-deuteriated ethyl iodide, indicated a difference in rates of over four orders of magnitude at 200 K [67]. The second, which focused on the identification of the regio-substitutions of hydrogen atoms in ethane during the catalytic H-D exchange between normal ethane and deuterium gas, estimated the β-/α-dehydrogenation rate ratio at only about five at 600 K, a more realistic temperature for reforming [69]. Again, these two pieces of evidence provide an estimate for the difference in activation energy between α- and β-hydride elimination of approximately 2 kcal/mol. Figure 5 displays an Arrhenius plot to illustrate how all these observations can be combined to suggest that the different rates in alkyl dehydrogenation may be close under realistic catalytic conditions, and that the regioselectivity of the initial dehydrogenation reaction from alkyl intermediates there may, therefore, be less well defined than under vacuum.

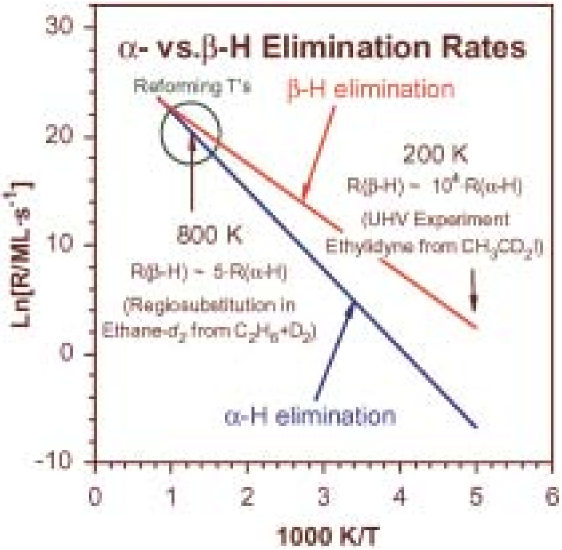

Figure 5. Schematic Arrhenius plot of the temperature dependence of α- and β-hydride elimination rates from adsorbed alkyl intermediates. β-hydride elimination is significantly faster than α-hydride elimination at the low temperatures in which most surface-science measurements are carried out [40]. However, α-hydride elimination also has a larger activation barrier, so the rate difference becomes smaller with increasing temperatures. On Pt(111), the R_α/R_β ratio changes from $\sim 10^{-4}$ at 200 K to about 0.2 at 800 K [28, 69]. The latter is a temperature more in tune with those used in catalytic reforming processes.

Hydrogenolysis (C–C bond-scission) after α-hydride elimination has been corroborated in the case of neopentyl iodide conversion on Ni(100) [40, 78]. In that system, the initial elimination of one of the α-hydrogen atoms from the neopentyl moiety occurs below 200 K, producing a stable neopentylidene intermediate that only reacts further above 350 K to ultimately produce isobutene. The mechanism by which neopentylidene decomposes to isobutene appears to involve the concerted scission of the C_α–C_β bond in conjunction with the elimination of hydrogen atoms from the α- and γ-positions. The interesting observation in terms of selectivity in reforming is that the hydrogenolysis of alkyl intermediates may be rate-limited by the C–C bond breaking step, but is decided by a much earlier and facile α-dehydrogenation reaction. In terms of γ-hydride elimination, the step probably responsible for the isomerization products, its occurrence appears to be not viable on nickel, but has been detected on platinum surfaces [90–93]. This observation explains the unique ability of platinum to catalyze reforming processes as opposed to nickel, which leads to exclusive cracking instead [40]. Again, it is the relative rates among the different available paths on a given surface that matter in terms of defining selectivity. All dehydrogenation steps follow the same qualitative trends, that is, they become faster on early transition metals or with heavier hydrocarbon chains, but the relative rates for α-, β-, and γ-dehydrogenations within the same metal also change across the periodic table. It is this change in relative dehydrogenation rates that explains the different performance of different metals in hydrocarbon reforming in terms of selectivity.

3. Role of carbonaceous deposits

The chemistry described above has been characterized using model systems, typically single crystals, and ultrahigh vacuum conditions. A question arises concerning the relevance of the conclusions derived from that work to actual catalytic processes carried out with complex solids and under atmospheric pressures. The resolution of this issue is particularly important in hydrocarbon conversion, where the working catalyst is not a pristine clean metal surface, but rather one covered with a complex layer of strongly adsorbed hydrocarbon residues [14, 94–96]. This carbonaceous layer is fast deposited on the surface by thermal decomposition of unsaturated hydrocarbon products of hydride eliminations from alkyl and other intermediates. In the case of olefins, the end products are alkylidyne species [60, 97–101], most likely from dehydrogenation of alkylidene intermediates [89, 102–104].

Some indirect evidence suggests that alkylidynes may be directly involved in demanding hydrogenolysis and reforming reactions [69, 105]. For mild catalytic processes such as olefin hydrogenation, however, strongly bonded carbonaceous species are likely to play only an indirect role [8, 18, 28]. In particular, temperature-programmed desorption and ^{14}C radioisotope labeling experiments have indicated that their residence time and composition may depend on temperature, becoming more hydrogen deficient and more strongly held with increasing temperature [106], but that they always turn over at rates orders of magnitude slower than those of most catalytic hydrogenations (figure 6) [60, 97, 107]. Perhaps the most important contribution of these carbonaceous deposits to the catalytic cycle is to temper the high activity of the clean metal, thus modifying the chemisorption characteristics of the reactants. This is particularly clear with unsaturated hydrocarbons, for which a new π bonding state becomes available [108–112]. Molecular beam kinetic work carried out in our laboratory has revealed that the π-bonded species are in fact the ones directly involved in catalytic hydrogenation processes (figure 7) [70, 113].

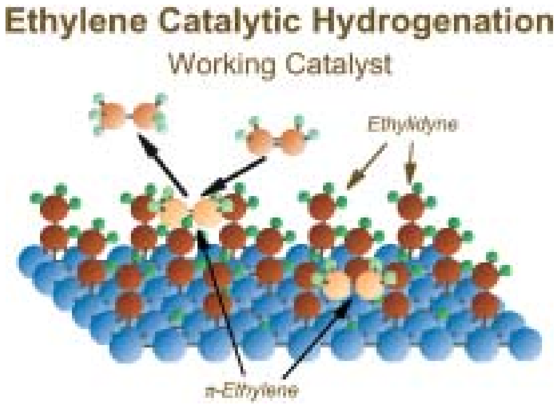

Figure 6. Relative turnover frequencies for surface reactions relevant to the catalytic hydrogenation of ethylene on Pt(111) single crystal surfaces. These data indicate that while ethylidyne formation on the clean metal is facile, its removal is not [60, 106]. Both hydrogenation of and H-D exchange within those moieties are several orders of magnitude slower than the catalytic hydrogenation of ethylene to ethane. It must be concluded that ethylidyne, although present during catalysis, does not participate directly in the hydrogenation mechanism. Also shown by the data is the fact that it is possible for catalytic kinetics to be emulated reasonably well with molecular beams under controlled vacuum conditions [70].

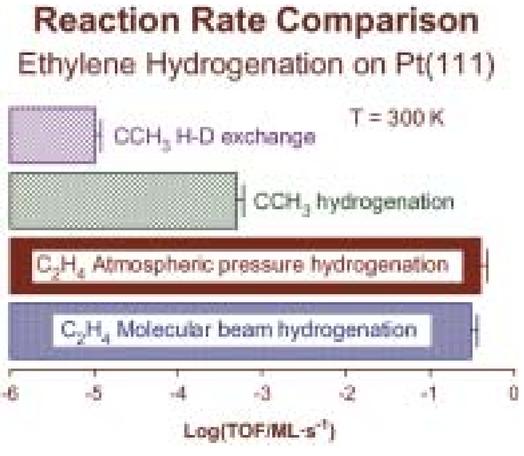

Figure 7. Schematic representation of the working surface during ethylene hydrogenation over Pt(111) single crystals. Upon exposure to the reaction mixture, the clean metal is rapidly covered with an ordered (2×2) layer of strongly adsorbed ethylidyne moieties [97]. A new weakly bonded π-state then becomes available for ethylene, allowing for its hydrogenation to ethane rather than its dehydrogenation to ethylidyne or other surface by-products [113]. This case provides a specific example of how the carbonaceous layer present during hydrocarbon reforming passivates the metal catalyst and thus opens new avenues for mild reactions.

Figure 8 schematically shows how all the preceding observations may come together to explain the performance of hydrocarbon reforming catalysts. As stated above, the working catalyst is covered with a strongly held hydrocarbon layer. This layer often displays a complex structure that includes both regions with three-dimensional growth and uncovered bare metal patches [16, 114]. Incoming alkane molecules are initially activated and converted into alkyl intermediates by metal atoms either in the exposed metal sites or on thinly covered patches. The majority of those alkyl surface species then undergo rapid and reversible β-hydride elimination, the route responsible for the fast alkane–alkene equilibria attained during the catalytic reforming. Since these are mild and rapid reactions, they most likely take place on surface areas modified by the carbonaceous deposits. On occasion, however, some

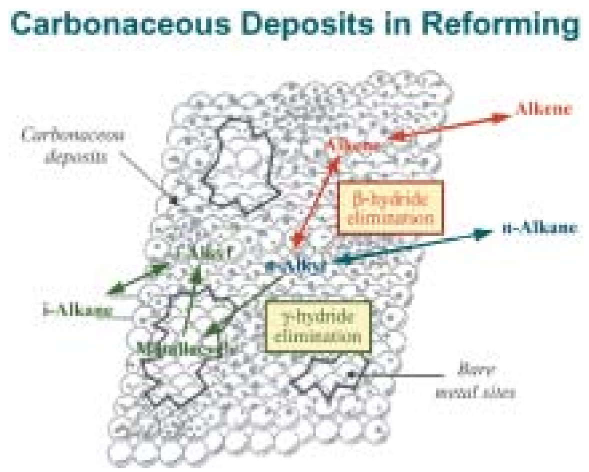

Figure 8. Overall picture of the network of key reaction steps involved in hydrocarbon catalytic reforming and of the nature of the working catalytic surface [16, 18]. Typically, alkanes are first activated by the metal to yield adsorbed alkyl intermediates. Subsequent mild hydrogenation and dehydrogenation steps, including the β-hydride elimination responsible for olefin production, take place on areas covered by carbonaceous deposits, which act as a passivator to inhibit extensive decomposition. On the other hand, α- and γ-hydride elimination, the more demanding steps responsible for hydrogenolysis and isomerization/cyclization, respectively, take place on patches of bare metal.

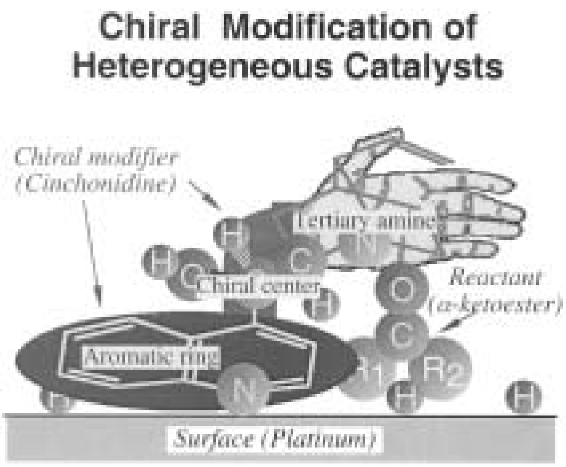

Figure 9. Schematic representation of the way cinchona chiral modifiers are believed to impart enantioselectivity to regular hydrogenation catalysts [149]. The working hypothesis is that the nitrogen in the quinuclidine moiety, a tertiary amine, forms a 1 : 1 complex with the reactant, an α-keto ester in this case, while the quinoline fragment, an aromatic ring, facilitates the adsorption on the (platinum) surface. The chiral center of the cinchona then selectively exposes one face of the carbonyl group of the reactant exclusively for hydrogenation. Studies in our laboratory indicate that the performance of this system is defined by the adsorption characteristics of the cinchona on the platinum surface [120–122, 125].

alkyl fragments may undergo α- or γ-hydride elimination instead, in which case alkylidene or metallacycle intermediates may form. These reactions, being more demanding, are likely to occur on uncovered metal sites, follow the same chemistry seen under vacuum [2], and eventually lead to the production of hydrogenolysis and isomerization/cyclization products respectively.

4. Chiral modification

One of the conclusions that arise from our above discussion is that carbonaceous deposits modify the behavior of hydrocarbon conversion catalysts. This modification can be seen as unintentional, since the carbonaceous deposits build up on the surface because of the decomposition of the reactants on the clean metal at the start of the catalytic process. However, catalytic surfaces can also be modified intentionally. There are indeed many examples where industrial processes rely on the use of additives either to affect the electronic properties of the catalyst (as with the addition of chlorine to reforming catalysts [14]) or to stabilize a particularly active solid phase (as with the use of lanthana to improve the aging properties of three-way catalysts in automobile catalytic converters [115]).

A more subtle approach to the modification of catalysts has been advanced recently for enantioselective hydrogenation reactions [116, 117]. The idea is to make use of small amounts of a chiral molecule to impart chirality to what is intrinsically an achiral surface. Perhaps the best documented example of this involves the addition of small amounts of cinchona, a family of naturally occurring chiral alkaloids, to α-keto ester solutions for their enantioselective hydrogenation to the corresponding α-hydro ester over supported platinum catalysts [118, 119]. It has been proposed that while the quinuclidine moiety (a tertiary amine) of the cinchona forms a complex with the α-keto ester, its quinoline fragments (an aromatic ring) aid in the adsorption to the surface (figure 9). The chiral center of the cinchona modifier then forces the selective incorporation of the hydrogen atoms onto only one of the two faces of the carbonyl group of the ester.

We in our laboratory have developed an *in-situ* infrared spectroscopy setup to investigate the molecular details of this modification at the liquid–solid interface where the chemistry takes place [13, 120]. Our work so far has indicated that the performance of the cinchona-modified platinum system is mainly controlled by the characteristics of the adsorption of the modifier itself on the metal. For one, optimal enantioselectivity appears to correlate with an adsorption geometry in which the aromatic quinoline ring lies flat on the surface [121, 122]. Interestingly, that adsorption geometry is affected by the concentration of the modifier in solution, so flat adsorption is seen at intermediate concentrations but a tilted geometry dominates at higher concentrations. The end result is that, perhaps counter-intuitively, the best performance is obtained with moderately low amounts of the cinchona modifier in solution [123, 124]. In another set of studies in our laboratory, it was determined that the catalyst needs to be pretreated with hydrogen in order to allow for the adsorption of the cinchona [125], but the extended exposures of the adsorbed cinchona layer to hydrogen lead to its removal via hydrogenation reactions [125]. Again, these observations correlate well with what is observed during catalysis [126–128]. Finally, the adsorption of cinchona and the activity and enantioselectivity of the cinchona/platinum catalyst correlate equally well with both the polar character of the solvent and the solubility of the chiral modifier in it [129–131].

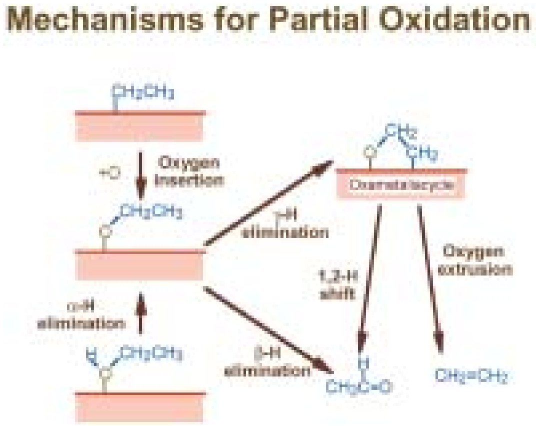

Figure 10. Schematic representation of the mechanistic steps that define the selectivity between dehydrogenation and dehydration in alcohols [7]. The key intermediate in this case is an alkoxide group, the result of α-dehydrogenation from adsorbed alcohols. In fact, the same intermediate may form by oxygen insertion into the metal–carbon bond of adsorbed alkyls during alkane oxidation. As with hydrocarbon reforming, the selectivity of both catalytic processes here appears to be defined by the regioselectivity of the next dehydrogenation step. Direct β-hydride elimination to aldehydes or ketones (the dehydrogenation products) is the preferred pathway on late transition metals. However, promotion of γ-hydride elimination, either by blocking or by altering the electronic characteristics of the β-carbon, leads to the production of an oxametallacycle, which can then undergo oxygen extrusion to the olefin (the dehydration product).

5. Selectivity in hydrocarbon and alcohol oxidation

The ideas discussed above in connection with hydrocarbon reforming catalysis can be easily extended to other systems. Specifically, we in our laboratory have been exploring the implications of the regioselectivity of dehydrogenation steps to the partial oxidation of hydrocarbons [7, 47, 132–138]. The balance between dehydrogenation and dehydration in organic alcohols, in particular, provides a classical example of the central role that kinetics play in controlling selectivity in catalysis: while acidic oxides such as γ-alumina often promote alcohol dehydration, basic oxides such as magnesia and calcium oxide typically favor alcohol dehydrogenation instead [139, 140]. The oxidation of alkanes is also closely connected to that of alcohols, because they both appear to involve the same initial alkoxide intermediates [7, 141]. As illustrated in figure 10, this key initial intermediate may form either via direct dehydrogenation of adsorbed alcohols at the hydroxo position [142], or by oxygen insertion into metal–alkyl bonds after alkane activation [135].

The dehydrogenation of alcohols to aldehydes or ketones has already been reported in a number of surface-science studies with late transition metals [7, 50, 143, 144]. In those, isotopic labeling experiments have been used to demonstrate that the reaction occurs via direct β-hydride elimination from alkoxides (figure 10) [132, 145]. Alcohol dehydration, on the other hand, often involves acid–base chemistry similar to that known in homogeneous organic reactions [146, 147]. However, it is conceivable to induce alcohol dehydration on nonacidic solids by forcing the alkoxide intermediate to undergo γ-hydride elimination and form a surface oxametallacycle (figure 10). A couple of recent experiments in our laboratory attest to the feasibility of this idea. In the first, a partial switch in mechanism for the partial oxidation of 2-propanol on a nickel surface, from acetone to propene formation, was achieved by substitution of the γ-hydrogens of one terminal methyl group with more electronegative fluorine atoms [137]. In the second, an oxametallacycle was prepared on the surface directly by thermal activation of a halo-alcohol [47]. The chemistry of that cyclic intermediate proved to be quite complex, but to include an oxygen extrusion step leading to the production of an olefin (figure 10). Together, the sequence of γ-hydride elimination and oxygen extrusion steps may account for alcohol dehydration processes. In that context, selectivity between dehydrogenation and dehydration of alcohols can be seen as dependent on the relative rates of β- versus γ-hydride elimination from surface alkoxides, in the very same way as the regioselectivity of the dehydrogenation of alkyl intermediates determines selectivity in hydrocarbon reforming. The idea of regioselectivity in early dehydrogenation steps defining catalytic selectivity may very well be quite general. It is important to also highlight that those are often not the steps that define total activity.

6. Concluding remarks

We conclude by reiterating the main point made in the introduction, that selectivity in catalysis is not necessarily defined by the same reaction steps that control total activity. We have illustrated this point above by elaborating on the mechanistic details of hydrocarbon conversion processes. It was shown that while activity here is often controlled by the initial activation of the alkanes in the reaction mixture, selectivity is typically defined by subsequent dehydrogenation steps. Elimination of hydrogen atoms from the β-position is clearly preferred on most alkyl surface intermediates, and explains fast alkane–alkene equilibria, double-bond migration, and H-D exchange reactions. Reforming, however, involves isomerization, cyclization, and aromatization reactions, and these are likely to require hydride elimination at the γ-position instead. Finally, hydrogenolysis, an undesirable side reaction, is led by α-hydride elimination. Therefore, by controlling the regioselectivity of the hydride elimination steps from surface intermediates early in the reaction mechanism, it is possible to seal the faith of hydrocarbon conversion processes. This idea appears to be quite general, also extending to partial oxidation reactions.

It was also said that the conclusions derived from surface-science studies using model systems can be extrapolated to the understanding of catalysis as long as this is done carefully. For instance, in hydrocarbon conversion, it is imperative to realize that the surface of the working catalyst is not the clean metal, but rather a metal partially covered with a complex network of strongly bonded hydrocarbons. The net effect of this carbonaceous layers is to passivate the high activity of the metal, providing new, weaker, adsorption states such as olefin π-bonding for the promotion of mild reactions, including the β-hydride elimination from alkyl intermediates responsible for the hydrogenation–dehydrogenation steps between alkanes and alkenes. At the same time, the remnant patches of exposed metal atoms allows for more demanding reactions, the α- and γ-hydride elimination steps that lead to reforming products, to occur still.

Lastly, it was mentioned that surface modification may be introduced in catalytic systems in a controlled manner. In particular, the use of chiral modifiers to add enantioselectivity to regular hydrogenation processes offers a promising new route for the synthesis of many pharmaceutical and agricultural products. This modification, however, is quite complex and requires a better basic mechanistic understanding before molecular-level designing can be accomplished. Our studies of these systems so far indicate that the performance of chiral-modified catalysts may be controlled by the adsorption characteristics of the modifier itself.

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