Tuning selectivity in hydrocarbon conversion catalysis ☆

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Abstract

An argument is made here for the importance of the kinetics of surface reactions in determining selectivity in catalytic processes. Particular emphasis is given to hydrocarbon conversion. Three examples from our research are used to illustrate how such selectivity can be tuned by changing the nature of the catalyst, by altering specific molecular features of the reactants, and/or by tuning the reaction conditions. Our discussion starts with the role of regiospecificity in dehydrogenation steps from adsorbed hydrocarbon intermediates in reforming, by showing how β-hydride elimination can explain hydrogenation, double bond migration and *cis–trans* isomerization in olefins. Next, the role of similar dehydrogenation steps in partial oxidations is illustrated by an example where atomic substitutions within the reactants can tip the balance between β- and γ-hydride elimination rates, and with that the selectivity between dehydrogenation and dehydration products from alcohols. Finally, the use of cinchona chiral modifiers to impart enantioselectivity to platinum hydrogenation catalysts is explained, and the role that reaction conditions such as concentrations, dissolved gases, and the nature of the solvent play in defining the performance of those systems is interpreted by using a molecular picture of the adsorption of the modifier.
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1. Introduction

The underlying principle behind chemical catalysis is the ability of the catalyst to modify the kinetics of the reaction being catalyzed [1–3]. Typically, catalysis is viewed as a way to accelerate chemical processes to make them commercially viable [4]. As industrial manufacturing has become more sophisticated, however, increasing demands have been placed on improving the selectivity of catalytic processes instead. Indeed, economical and environmental considerations have imposed the need for highly selective catalysis in order to reduce reactant consumption, minimize separation processes, and avoid the need for expensive clean up and disposal of unwanted byproducts [5].

The selectivity of catalytic processes, like their overall activity, is defined by the kinetics of the reactions involved. However, the parameters that control selectivity are typically more sensitive and difficult to adjust than those defining the total rate [6]. This is illustrated by the energy diagram provided in Fig. 1. There, it is seen that the high initial barrier $\Delta G^{\ddagger}_{rls}$ for the conversion of the reactant to the intermediate limits the turnover frequency of the overall process. On the other hand, it is the difference in activation barriers from the intermediate to each of the two possible products, $\Delta G^{\ddagger}_1 - \Delta G^{\ddagger}_2$, that defines selectivity. The criteria for lowering $\Delta G^{\ddagger}_1$ with respect to $\Delta G^{\ddagger}_2$ are not likely to be the same as those required to modify $\Delta G^{\ddagger}_{rls}$.

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. From a practical point of view, changes can be exerted on the catalyst itself, on the reactants, and/or on the reaction conditions. However, in order to be able to predict selectivity in catalysis, a better understanding of the mechanisms of the underlying chemical reactions is needed. We in our laboratory have been studying a number of reaction mechanisms on model systems in order to address these kinetic issues [7–10]. Our approach has been to isolate key surface intermediates and to study their elementary reactions by
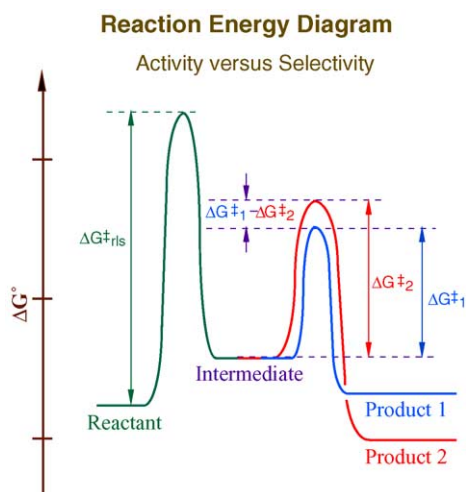
Fig. 1. Simplified energy diagram for catalytic processes illustrating the different criteria needed to optimize total reactivity vs. selectivity [16]. It can be seen that while the overall rate is controlled by the energy barrier of the initial conversion of the reactant into the intermediate, $\Delta G^{\ddagger}_{rls}$, the selectivity, defined as the yield ratio of product 1 to product 2, is determined by the difference in barrier heights $\Delta G^{\ddagger}_1 - \Delta G^{\ddagger}_2$ for the two subsequent reactions available to the intermediate. Notice that a relative variation of only 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 [6].

using a combination of modern surface-sensitive techniques [11,12]. Below we cite a few examples from this work, and suggest some implications of the basic kinetic knowledge acquired to the design of new and better catalysts. Our focus will be on hydrocarbon conversion.

2. Nature of the catalyst

The first example refers to the reactions responsible for hydrocarbon reforming, as used in petroleum refining [13,14]. It is widely accepted that the rate-limiting step in these processes often is the initial dissociative adsorption of the alkanes in the original feedstock, a reaction that requires the activation of a C–H bond and presumably leads to the formation of the corresponding chemisorbed alkyl intermediates [15]. On the other hand, we believe that selectivity in reforming is defined by the regioselectivity of the first hydrogen abstraction from those surface alkyl species [7,16]. Specifically, the preference for dehydrogenation of adsorbed alkyl intermediates at the β position has been indicated by experimental results from our group [17–20].

β-Hydride elimination directly accounts for the fast production of olefins during reforming that commonly leads to the establishment of rapid alkane–alkene equilibria [21,22], and also explains H–D exchange and double-bond migration reactions [23–28]. An example of the type of data supporting this conclusion is shown in Fig. 2 [29]. In that case, temperature programmed desorption (TPD) experiments were used to probe the ease and extent to which 2-butyl groups undergo H–D exchange on platinum surfaces. The results are easier
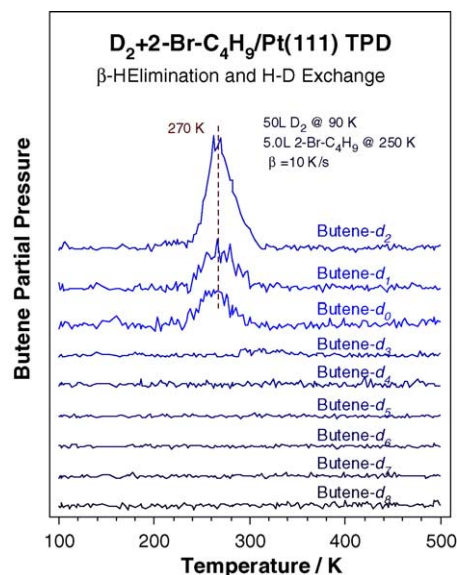

Fig. 2. Temperature-programmed desorption (TPD) data for the desorption of (deuterated) butene from activation of adsorbed 2-bromo butane on a deuterium-predosed Pt(1 1 1) surface [29]. The surface was first presaturated with 50 L ($1\,L = 1 \times 10^{-6}$ Torr s) of D_2 at 90 K, then exposed to 5.0 L of the halohydrocarbon at 250 K to ensure the scission of the C–Br bond and the formation of surface 2-butyl groups [18]. Subsequent β-hydride elimination from those intermediates yields normal butene [17], and further alkyl–alkene interconversions allows for the H–D exchange responsible for the production of the deuteriated butenes [27]. The fact that not more than two hydrogen atoms are replaced by deuterium points to the fact that β-hydride elimination is favored from internal carbon atoms, and that the resulting olefin is most likely 2-butene.

to understand in view of the accompanying energy diagram provided in Fig. 3. First, 2-butyl surface groups, prepared by thermal activation of 2-bromo butane [18,30], can undergo β-hydride elimination at either the first or third atoms in the
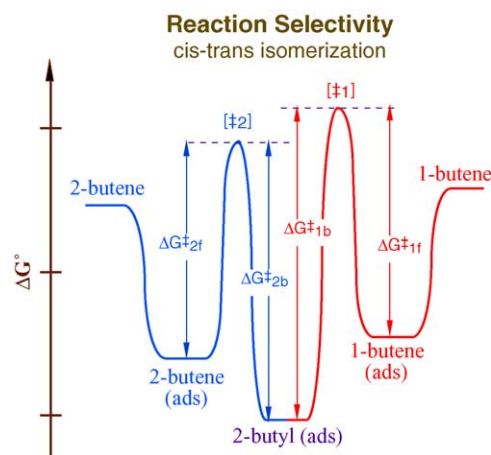

Fig. 3. Energy diagram for the catalytic migration of double bonds in olefins. The example shown is that of butene, to explain the experimental data in Fig. 2. A common 2-butyl surface intermediate undergoes selective β-hydride elimination at the inner (C_3) carbon to yield 2-butene because of the lower barrier compared to that of dehydrogenation at the terminal (C_1) carbon. A more complex diagram that includes the stereoselectivity of the hydrogen removal can also account for *cis–trans* isomerizations [34].

carbon backbone, to yield either 1- or 2-butene, respectively. The present experiments cannot differentiate between those two products directly, but additional work with longer chains has proved the preference towards elimination at the inner carbons [31,32]. In fact, that is indicated here indirectly by the fact that only a maximum of two hydrogens can be exchanged per butyl intermediate, presumably those bonded to the central carbon atoms in 2-butene. This H–D exchange takes place via a reversible double-bond insertion into the metal hydrogen bond that hydrogenates adsorbed butenes back to 2-butyl surface species (the reverse of the β-hydride elimination step) [33,34]. Thanks to both a marked kinetic isotope effect and the stereospecificity of the β-hydride elimination step, a study of double-bond migration and *cis–trans* isomerization reactions is also possible in this system. That work is under way.

In spite of the ease with which β-hydride elimination takes place, dehydrogenation steps at other positions in the hydrocarbon chain are still required to account for more demanding reforming processes. Inspection of past studies on supported catalysts has led to the suggestion that while hydrogen removal at the γ carbon may be responsible for desirable isomerization and cyclization steps [35–37], dehydrogenation at the α position is likely to end in the production of undesirable hydrogenolysis products instead [38]. In fact, we have obtained direct evidence for C–C bond scission in neopentyl groups adsorbed on nickel following α-hydride elimination to yield isobutene [39]. No similarly clear proof is yet available for a γ-hydride elimination leading to isomerization products, but better selectivity towards that step has become evident on platinum compared to nickel [40,41]. It is tempting to ascribe the unique performance of platinum-based catalysts in reforming to their ability to promote dehydrogenation at the gamma position. This would indicate that selectivity in reforming is defined by the regioselectivity of the first hydrogen removal from surface alkyl intermediates, as mentioned above, and that such selectivity could be tuned by modifying the electronic and/or structural characteristics of the catalyst [10].

3. Nature of the reactants

A second example on how selectivity in catalysis can be better understood by characterizing the mechanism of the reactions involved comes from the surface conversions associated with the oxidation of alkanes and alcohols [8]. It does appear that, on late transition metals, atomic oxygen may easily insert into metal–alkyl bonds (in alkyl intermediates produced by surface activation of alkanes) to produce alkoxide surface species [42,43]. Similar intermediates can be produced by dehydrogenation of adsorbed alcohols at the hydroxo position [44]. Those alkoxides then dehydrogenate further upon thermal activation, again preferentially at the beta position, to produce aldehydes or ketones [45]. Nevertheless, suppression of the latter step may allow hydrogen removal at the gamma position, and to the concomitant formation of a surface oxametallacycle intermediate. Such an intermediate may then undergo oxygen extrusion to produce an olefin [46–48].

One way to favor γ- over β-hydride elimination in these systems is by using electron-withdrawing substitutions to destabilize the positive charge that forms at the beta carbon during β-H elimination [49]. This approach does indeed work quite well in the case of 1,1,1-trifluoro-2-propanol on nickel, the thermal activation of which results in significant amounts of propene production [50]. A related case is that of the competition between the breaking of a carbon–heteroatom bond in *tert*-butyl-based intermediates and hydride elimination at the gamma position. Fig. 4 displays TPD data for the production of isobutene on Ni(1 0 0) as a function of the nature of the heteroatom, X, in such tertbutyl species, and Fig. 5 provides the corresponding energy diagram. When the C–X bond is weak, as is the case with the halides, that bond breaks first and leads to the formation of surface isobutyl intermediates, which then undergo fast β-hydride elimination to isobutene
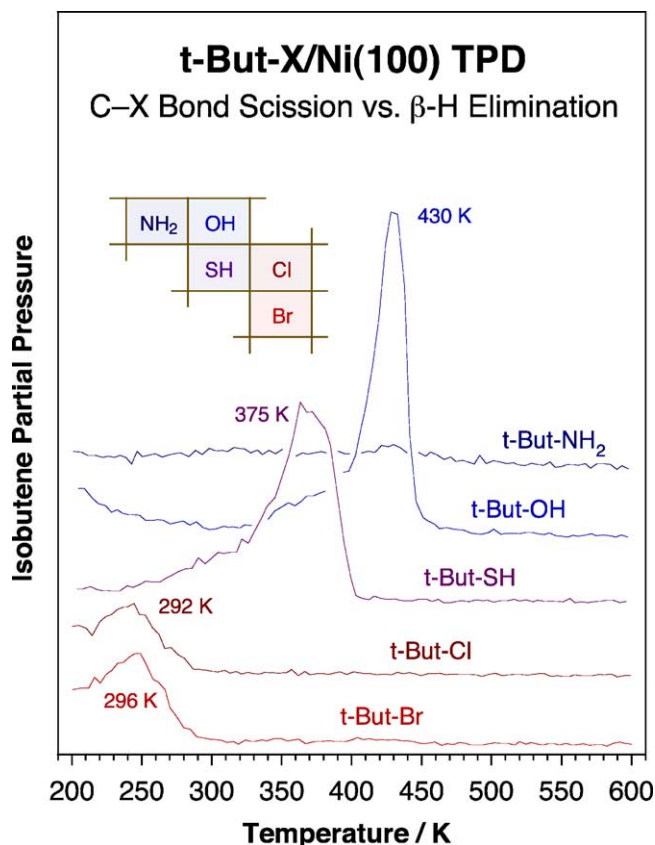

Fig. 4. Isobutene TPD from different *tert*-butyl derivatives adsorbed on Ni(1 0 0) as a function of substituent group (X) [48]. Data are reported here for *tert*-butyl bromide, chloride, thiol, alcohol, and amine. Both the yield of the resulting isobutene and its temperature of desorption are significantly affected by the nature of the substituent. The desorption temperature in particular reflects the energetics of the rate-limiting step of this conversion, which changes from β-hydride elimination in *tert*-butyl surface moieties with the halides (after the scission of the C–X bond) [41], to the C–X bond-breaking in the thiol, alcohol, and amine [50]. This latter scission may be preceded by a γ-hydride elimination step.
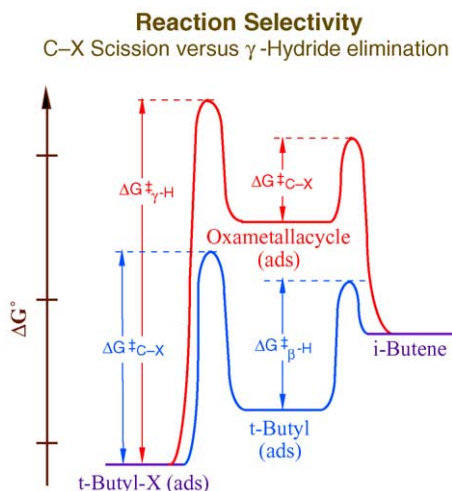
Reaction Selectivity
C–X Scission versus γ-Hydride elimination

Fig. 5. Energy diagram for the activation of *tert*-butyl–X adsorbed fragments on metals, to account for the results in Fig. 4. Two competing pathways, C–X bond-scission vs. γ-hydride elimination, set the selectivity towards alkyl vs. oxametallacycle intermediate formation, respectively, and with that the ease with which isobutene is produced. Easy C–X bond breaking is seen with the halides, but γ-hydride elimination takes over in the cases of the alcohol, thiol, and amine.

[39]. However, in cases such as alkoxides, where the C–X (C–O) bond is stronger, the olefin is produced at much higher temperatures. This can be explained by a reversal in the sequence of the elementary steps responsible for the conversion: a γ-hydride elimination takes place first, and is followed by oxygen extrusion from the resulting oxametallacycle. The case with the thiol shows some intermediate kinetics, and the isobutene yield with the amine is almost undetectable. Note that in the examples cited in this paragraph, changes in selectivity were induced by specific substitutions in the reactant molecules.

4. Catalytic conditions

Finally, selectivity in catalysis can also be controlled by tuning the conditions used to carry out the reaction. This can be nicely illustrated by the case of the hydrogenation of α-ketoesters to α-hydroxyesters on cinchonidine-modified platinum catalysts. Platinum alone is well known to promote hydrogenation for this type of reaction, but cannot provide any enantioselectivity even if a prochiral reactant is employed, and yields a racemic mixture of products instead. However, if enantiomerically pure products are desired, chirality can be bestowed on the surface by the addition of small amounts of cinchona modifiers [51]. Such chiral modification can be explained using the energy diagram provided in Fig. 6. Since the carbonyl function of the reacting α-ketoester is planar, there is no expected preference for either side of the molecule to interact with the metal upon adsorption on the clean platinum surface. Consequently, the barriers for its hydrogenation to the *R* and *S* α-hydroxyesters are identical, and no enantiose-

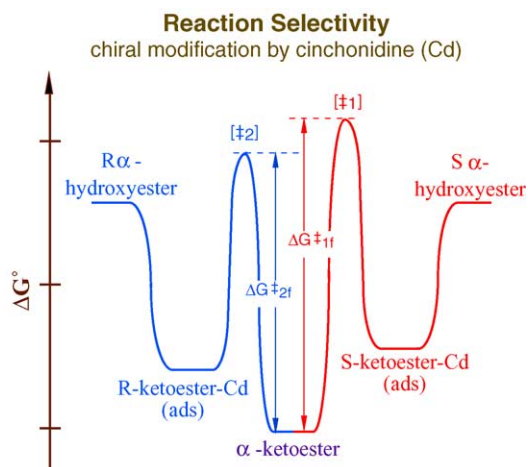**Reaction Selectivity**
chiral modification by cinchonidine (Cd)

Fig. 6. Energy diagram for the chiral modification of platinum surfaces by adsorbed cinchonidine. Hydrogenation of α-ketoesters can be facilitated by platinum catalysts. However, if used alone, that metal affords a racemic mixture of *R* and *S* α-hydroxyesters. On the other hand, the addition of small amounts of cinchonidine – a natural chiral alkaloid – to the reaction solution imparts enantioselectivity to the hydrogenation process, presumably by favoring a specific adsorption geometry of the reactant via the formation of a complex with the modifier, and to the selective production of only one of the α-hydroxyester enantiomers [52,66]. This chiral modification is highly sensitive to the conditions of the reaction, and depends strongly on parameters such as chiral modifier concentration [53], adsorbed gases [57], and the nature of the solvent [61].

lectivity is obtained. On the other hand, the preadsorption of a chiral modifier such as cinchonidine can break this symmetry by favoring the formation of a complex with a specific geometry defined by its chiral center, thus lowering the activation barrier towards one of the two enantiomers. Unfortunately, the performance of these systems is highly dependent on the conditions used to carry out the reaction. The lack of understanding of this relationship between reaction conditions and catalytic performance has so far severely limited the application of chiral modification for practical industrial synthesis.

Recent experiments in our laboratory have indicated that many of the trends observed in the activity and selectivity with cinchona-modified platinum catalysts can be traced to the nature of the adsorption of the modifier on the surface [52]. For instance, optimal enantioselectivity appears to correlate with an adsorption geometry where the aromatic quinoline ring lies flat on the surface [53,54]. Interestingly, that geometry is affected by the concentration of the modifier in solution: 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 [55,56]. In another set of studies in our laboratory, it was determined that the catalyst needs to be pre-treated with hydrogen in order to allow for the adsorption of the cinchona [57], but that extended exposures of the adsorbed cinchona layer to hydrogen lead to its removal via hydrogenation reactions [57]. Again, these observations correlate well with what is observed during catalysis [58–60].
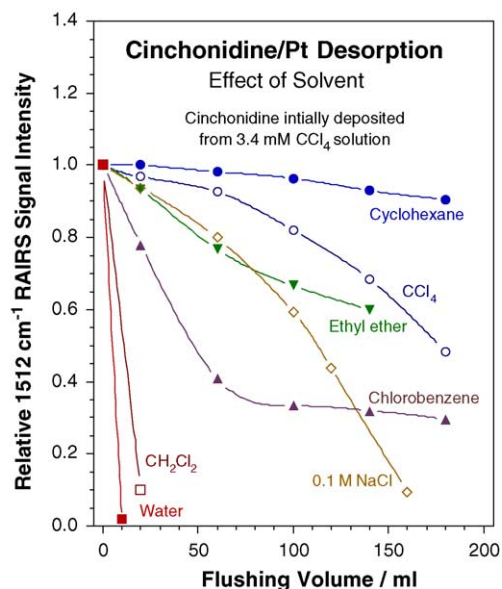
Fig. 7. Desorption of adsorbed cinchonidine vs. rinsing volume as a function of solvent [61]. In these experiments, the cinchonidine was first adsorbed from a carbon tetrachloride solution saturated with cinchonidine onto a polished polycrystalline platinum disk, and then flushed with sequential 20 mL aliquots of the stated solvents. The remaining coverage of the adsorbate was determined in situ by following the infrared absorption signal at 1512 cm^{-1}, corresponding to an in-plane deformation of the quinoline ring [54], using a cell specifically designed to characterize these solid–liquid interfaces [67]. It is clearly seen here that the reversibility of the desorption is severely affected by the nature of the solvent, going from fast desorption with water and dichloromethane to virtually irreversible adsorption with cyclohexane and other alkanes. This trend correlates well with the ability of cinchonidine to impart chirality for enantioselective hydrogenation on platinum catalysts [52,66].

Fig. 7 summarizes the data obtained from our research on the effect of the nature of the solvent on these systems [61]. Clearly, the reversibility of the adsorption of cinchonidine from solution onto the platinum surface is greatly affected by the polarity of the solvent used, and goes from rapid desorption on water and dichloromethane to almost complete irreversibility with most saturated organic solvents. Once again, these trends are mirrored by the performance of the catalyst [62,63]. More studies are underway to better understand the molecular-level behavior of this cinchona-platinum system, but it is already clear that the performance of the catalyst is closely related to the adsorption characteristics of the chiral modifier, and that this, in turn, depends strongly on and can be tuned by varying the reaction conditions used.

5. Concluding remarks

The three examples from our studies discussed above provide only a glimpse of what we and others have been able to accomplish by using modern surface-science technology to study reactivity in model systems relevant to catalysis [11]. The objectives in this report have been to point out that selectivity is often a more important parameter to consider when designing catalysts than total activity, and that those are not necessarily defined by the same reactions steps. It has also been our intention to highlight the fact that, difficult as it may be to tune selectivity because of the mechanistic subtleties involved, many parameters are available for this task, including the nature of the catalyst, the reactants, and the reaction conditions. Changes can be and often are made to alter the energetics of surface reactions, but entropic variations can also be introduced, as illustrated by our example on chiral modification (where optimization of the transition state is in part obtained by restricting adsorption geometries), and also by the well-known use of shape selectivity with zeolites.

It may be thought that the model systems often used in studies with modern surface-sensitive techniques are quite removed from the real catalytic systems used in industry, but continuing work by many groups has indicated that the connection between the two can in fact be reasonably made as long as a number of key factors are taken into account [16]. 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 that is partially covered with a complex network of strongly bonded hydrocarbons [7,64,65]. The net effect of this carbonaceous layer is to passivate the high activity of the metal, providing new, weaker, adsorption states such as π bonding in olefins. These, in turn, facilitate mild reactions like the β-hydride elimination from alkyl intermediates responsible for the hydrogenation-dehydrogenation steps that lead to the interconversion between alkanes and alkenes [22,25]. At the same time, the remnant patches of exposed metal atoms allow for more demanding reactions, the α- and γ-hydride elimination steps that lead to reforming products. This idea can in fact be extended to broaden the way catalytic processes are designed by, for instance, introducing surface modification in a controlled manner. The use of chiral modifiers to add enantioselectivity to regular hydrogenation falls into this category. Ultimately, the underlying surface chemistry responsible for heterogeneous catalysis is closely related to that observed in model systems. Therefore, by performing detailed molecular-level studies on the mechanism of surface reactions using the new surface-sensitive tools at our disposal, it should be possible to advance the designing of catalysts.

Acknowledgements

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