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Probing catalytic reactions at surfaces

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Abstract

A review of the major contributions from modern surface science to the understanding of the chemistry of heterogeneous catalysis is provided. A number of basic concepts, including the nature of surface bonds, the dynamics of surface reactions, and the identification of the intermediates and elemental steps that comprise the catalytic processes, are surveyed. The localized nature of the surface chemical bond, the drastic changes that varying surface coverages introduce on surface energetics and kinetics, and the key role that subtle energy barrier differences among competing reactions play in defining the overall selectivity of catalytic processes are particularly noted. A discussion on the implications of these microscopic concepts to catalysis is then provided. A critical analysis of the limitations encountered when extrapolating results from well-defined model systems to more realistic reaction conditions using supported catalysts and on the ways those problems have been addressed is also presented. A more comprehensive summary of the knowledge acquired to date on the surface chemistry of hydrocarbon conversion reactions on transition metals is provided. Finally, some ideas on the future directions of surface science in connection with catalysis are advanced. © 2001 Elsevier Science Ltd. All rights reserved.

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Nomenclature

AES	Auger electron spectroscopy
AFM	Atomic force microscopy
APS	Appearance potential spectroscopy
ARUPS	Angle-resolved ultraviolet photoelectron spectroscopy
DFT	Density functional theory
ELS	Energy loss spectroscopy
ER	Eley–Rideal
ESDIAD	Electron-stimulated desorption ion angular distribution
EXAFS	Extended X-ray absorption fine structure
FIM	Field ion microscopy
GGA	Generalized gradient approximation
HREELS	High-resolution electron energy loss spectroscopy
INS	Ion neutralization spectroscopy
IR	Infrared
ISS	Ion scattering spectroscopy
LDA	Local density approximation
LEED	Low-energy electron diffraction
LH	Langmuir–Hinshelwood
MC	Monte Carlo
NEXAFS	Near-edge X-ray absorption fine structure
NMR	Nuclear magnetic resonance
PES	Photoelectron spectroscopy
PIES	Penning ionization electron spectroscopy
RAIRS	Reflection–absorption infrared spectroscopy
SEM	Scanning electron microscopy
SEXAFS	Surface extended X-ray absorption fine structure
SFG	Sum-frequency generation
SIMS	Secondary ion mass spectroscopy
STM	Scanning tunneling microscopy
STS	Surface tunneling spectroscopy
TEM	Transmission electron microscopy
TPD	Temperature-programmed desorption
UHV	Ultrahigh vacuum
UPS	Ultraviolet photoelectron spectroscopy
XES	X-ray emission spectroscopy
XPS	X-ray photoelectron spectroscopy

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1. Introduction

Catalysis is a mature field, expanding over almost two centuries [1]. The term catalysis was coined by Berzelius [2] in 1835 to refer to the observation by Davy around 1820 that platinum surfaces greatly facilitate the oxidation of hydrogen to water [3]. At that time, he defined catalysts as substances that increase the rate of chemical reactions without being themselves consumed in the process [1]. Nowadays, catalytic phenomena affect virtually all aspects of our lives. Enzymatic catalysis, for instance, constitutes the basis for most of the biochemistry associated with life [4]. In addition, more than 80% of the industrial chemical processes presently in use rely on one or more catalytic reactions [5]. The worldwide market of catalysts is valued at

about US\$ 10 billion, and industrial catalysis accounts for about one quarter of the world's gross domestic product (GDP) [6]. Catalysts are used for the processing of foods, the production of medicines, the refining of petroleum, the manufacture of synthetic fibers and plastics, and the synthesis of a wide range of other chemicals [7]. More recently, catalysis has also become a key player in the protection of the environment [8].

Most of the catalytic processes in existence today are heterogeneous in nature, typically involving solid catalysts and gaseous or liquid reactants. Since the initial discovery of the catalytic properties of platinum for hydrogen oxidation, a vast number of catalytic processes have been developed [9]. Some of the highlights of this illustrious history include the development in the 1880s of the so-called contact process for oxidizing sulfur dioxide to sulfur trioxide (a precursor for sulfuric acid) [10], the advancement in the 1900s of the Haber process for the production of ammonia from gas-phase nitrogen [11] and of the Ostwald process for the oxidation of ammonia to nitric oxide (a precursor for nitric acid) [12], and the introduction of the Fischer–Tropsch process for the production of synthetic fuels about 1923 [13], the Houdry catalytic cracking of hydrocarbons in 1936 [14], and the Ziegler–Natta catalysts for the polymerization of olefins in 1955 [15].

Surprisingly, most of the major advances in catalysis have been serendipitous, or, at best, a consequence of multiple empirical trials. That is not to say that there have not been scientific advances during the technological progress of catalysis. In fact, it is more appropriate to view both science and technology in this field as advancing hand in hand. A number of key discoveries in basic science have indeed helped shape further catalyst development. For instance, initial kinetic studies by Bodenstein and Oswald at the beginning of the century established that reactions can be catalyzed only if they are thermodynamically favorable, since any increase in rate in the forward reaction is accompanied by a corresponding increase in the rate of the reverse step [1]. By 1920, Sabatier [16] had suggested that catalytic hydrogenation is connected to the ease with which metals can dissociate and adsorb hydrogen. Later, Langmuir, Rideal, and Hinshelwood worked out the basics of the kinetics of adsorption and surface reactions [17]. Taylor [18] then introduced the idea of specific active sites on the surface, and pointed to the particular role played by surface defects in catalysis. Soon afterwards, Balandin [19] interpreted some catalytic behavior in terms of specific geometrical arrangements of atoms on the surface, what today is referred to as the ensemble effect. Additional ideas by Eley, Marshall, Beeck, Scwab, Bond, Horiuti, Polanyi, Wells, Ipatieff, and others also helped shape the theories behind heterogeneous catalysis, and with those the design of new catalytic processes.

Some beautiful kinetic work was indeed carried out in the early 20th century by the pioneers mentioned above. However, only the advent of spectroscopies, such as infrared and nuclear magnetic resonance (NMR) allowed for a more direct characterization of surfaces [20,21]. Infrared data in particular proved quite revealing, pointing to the localized nature of the adsorbate-surface bond [22]. That led to the extension of the theories used to explain chemical bonding in discrete molecules to catalysis [23,24]. At the same time, it became clear that the complex nature of heterogeneous catalysts makes the control of catalytic processes extremely difficult, and

that studies with model systems were necessary to unravel the role of each component to the overall behavior of catalysts. It was concluded that a detailed understanding of surface phenomena is indispensable for the systematic design of catalytic processes.

The development of new surface-sensitive techniques in the 1960s opened the doors to the microscopic basis of catalysis [25,26]. A large collection of spectroscopies became available for the study of both the structural and electronic details of surfaces and the nature and chemical reactivity of adsorbates [27,28]. Ultrahigh vacuum (UHV) technology provided added control of the experimental conditions under which the surfaces were to be studied [25]. The field of surface science, and more specifically the study of the surface science of catalysis, blossomed as a result. Although this is still a young area of research, many advances have already been made in terms of unraveling the fundamental aspects of surface reactions and identifying the key parameters for the development of new catalysts. This review provides an overview of the contributions of modern surface science to the understanding of catalytic processes, specifically those from experiments with single-crystal surfaces. Particular emphasis is placed on the discussion of basic kinetic issues, including the identification and characterization of relevant surface intermediates and the determination of the appropriate kinetic parameters for surface chemical conversions. Those kinetic ideas are then incorporated into a broader analysis of mechanisms in surface reactions. The relevance of the surface chemistry seen under vacuum to high-pressure catalytic processes is discussed. Finally, some future directions in this field of research are suggested.

2. Surface intermediates

Perhaps the most noticeable contribution of surface science to catalysis has been the isolation and characterization of surface adsorbates of potential relevance to heterogeneous catalysis. The large number of surface-sensitive techniques developed over the last decades has provided new tools for the detailed study of surface species [28,29]. In this context, diffraction techniques, such as low-energy electron diffraction (LEED) [30,31], atomic [32] and ion [33] scattering, photoelectron diffraction [34], and extended X-ray absorption fine structure (EXAFS) [35,36], can be used for the determination of surface structures. Additional local geometry can also be obtained by electron-stimulated desorption (ESD) [37,38], and by scanning and transmission electron (SEM and TEM) [39–41], field-ion (FIM) [42,43], and scanning tunneling (STM) and atomic force (AFM) [31,44–48] microscopies. Surface electronic structures can be probed by photoelectron (PES) [49,50], inverse photoemission [51–53], ion neutralization (INS) [54], Auger electron (AES) [27,55], appearance potential (APS) [28], energy loss (ELS) [56], near-edge X-ray absorption (NEXAFS) [57,58], X-ray emission (XES) [59], and penning ionization electron (PIES) [60] spectroscopies. Surface vibrational properties can be investigated with infrared (IR) [61–63], Raman [64], high-resolution electron energy loss (HREELS) [65], electron tunneling [66,67], and sum-frequency generation (SFG) [68] spectroscopies. Finally, surface chemical compositions can be determined by AES [55], temperature-programmed

desorption (TPD) [69–71], ion scattering (ISS) [33], and secondary ion mass (SIMS) [72,73] spectroscopies. Many studies using these and other techniques have greatly advanced our understanding of the nature of the interaction of adsorbates with solid surfaces.

2.1. *Surface chemical bond*

One of the early and most striking conclusions reached from modern surface-science studies is the fact that the chemical bonds between adsorbates and solid surfaces are, in general, quite localized. This had already become apparent during the infrared characterization of adsorbates on supported catalysts [22], but was clearly proven in diffraction studies with single-crystal surfaces. Initial LEED work indicated that, in most cases, adsorbed molecules order by following the registry of the substrate [74]. Further analysis of LEED intensity–voltage data established that the adsorbates adopt a well-defined bonding geometry on specific surface sites [75]. Other studies also revealed that most of the electronic and structural details of the free molecules are preserved upon adsorption on solid surfaces [49]. The implication from all these observations is clear: surface bonds are restricted to a small volume around the adsorption site. This is true even in the case of metals, where the conduction band spreads throughout the solid. Thanks to this localized nature of surface bonds, it has been possible to describe most surface–adsorbate systems in terms of similar chemistry with discrete molecules [24].

Clear parallels have, in particular, been identified between adsorbates on surfaces and ligands in organometallic complexes [76–79]. Early examples of this include the coordination of carbon monoxide to transition-metal centers, as in the case of CO bonded to iridium illustrated in Fig. 1. There, the photoelectron spectra of free CO, of an iridium carbonyl – $\text{Ir}_4(\text{CO})_{12}$ – cluster, and of CO adsorbed on an Ir(100) surface, are contrasted. In all three systems, the peaks corresponding to the 4σ and 1π orbitals of CO are seen at about the same binding energies, approximately 11.5 and 8.5 eV, respectively, an indication that those are non-bonding orbitals as far as the CO–metal interaction is concerned (the 4σ orbital has most of its electron density around the oxygen atom, the 1π orbital is the responsible for the double bond between the carbon and oxygen atoms). In contrast, the 5σ orbital, seen around 5.5 eV in the case of free CO, is not easily detected in either of the two coordinated systems, presumably because of its shift towards higher binding energies. This has been explained by the Chatt–Dewar–Duncanson model [80], known in surface science as the Blyholder model [23], and depicted schematically in the right diagram of Fig. 1. According to this picture, the bonding between the carbon monoxide molecule and the metal is accounted for by electron donation from the CO 5σ orbital, which has most of its electron density pointing outwards from the carbon atom, to the empty metal d orbitals, and by back-donation from filled metal d orbitals into the CO $2\pi^*$ antibonding orbital of the adsorbate. These interactions result not only in the higher binding energy for the 5σ orbital alleged in Fig. 1, but also in a partial filling of the $2\pi^*$ level. By using both variable photon energy [81] and angle-resolved ultraviolet photoelectron (ARUPS) [82,83] spectroscopies, it has been possible to extract the

Carbon Monoxide Bonding to Transition Metals

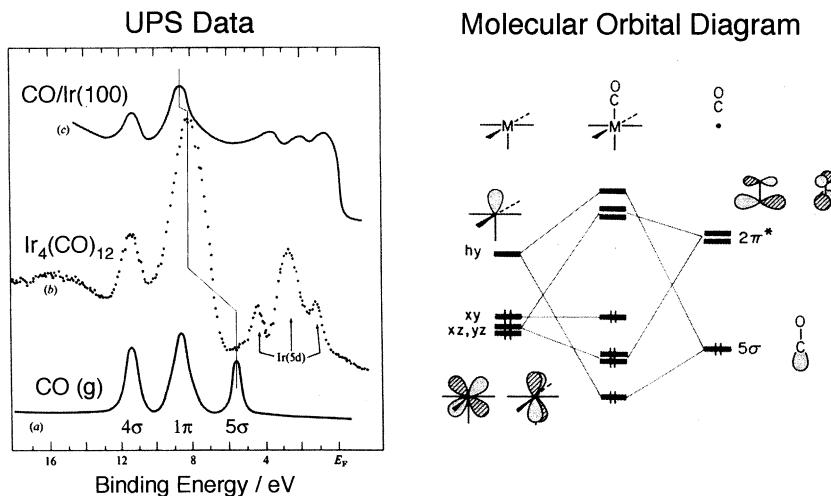


Fig. 1. Example illustrating the similarities in bonding between surface adsorbates and organometallic ligands. The left panel shows ultraviolet photoelectron spectra (UPS) for carbon monoxide in the gas phase (a), bonded to an iridium cluster (b), and adsorbed on an iridium surface (c) [930]. After appropriate rigid energy shifts, it is seen that the CO molecule undergoes a similar molecular rehybridization in both metal systems. The 5σ non-bonding orbital, centered around the carbon atom, becomes stabilized upon mixing with the d orbitals of the metal, and moves towards higher binding energies. The right-hand side diagram indicates how the energy levels change upon the formation of the corresponding molecular orbitals [24].

peak due to the 5σ photoelectrons from underneath the 1π orbital signal at about 8–9 eV binding energy. In addition, inverse photoemission [84], penning ionization [85], and two-photon photoemission [86] experiments have clearly identified the partially populated and energy-lowered CO $2\pi^*$ orbital. The Blyholder model of chemisorption is now well accepted, and has been extended to other unsaturated molecules such as NO, N_2 , and olefins.

The localization of surface–adsorbate bonds can also be tested from the point of view of the changes in the surface electronic states upon adsorption. That adsorbates alter the surface was perhaps first noticed by the fact that most saturated overlayers order in structures with unit cells larger than that of the substrate [87]. To mention but one example of this, chalcogen atoms tend to form (2×2) periodic lattices on most basal planes of transition-metal surfaces [25,88–90]. This overstructure is not due to steric effects, since oxygen atoms, for instance, are smaller than most transition metals. It is also not the result of kinetic limitations during adsorption, because the ordered structures persist upon annealing of the surface, and because similar superlattices are also seen with more mobile adsorbates, such as carbon monoxide [25]. Instead, the ordering of adsorbates in large unit cells has been explained by a combination of local electrostatic effects and longer-range electronic perturbations [91–96].

Adsorbate–adsorbate interactions can be either attractive or repulsive, and tend to alternate with distance. On the one hand, adsorbed molecules seldom bind to adjacent surface sites. On the other, they often form surface islands at low coverages. A classic example of this is the growth of oxygen monolayers on W(110), where (2×1) islands are formed at low coverages but both (2×2) and (1×1) phases are seen at higher coverages [97]. Such behavior can be understood in terms of repulsive first-neighbor and attractive second-neighbor O–O interactions. A number of theoretical approaches have been used to try to explain these observations in greater detail [94,98].

The nature of the interactions of adsorbates on surfaces has been tested extensively in the case of the effect of alkali metals on the chemistry of carbon monoxide. Both the C–O stretching frequency and the adsorption energy of CO adsorbed on transition metals are greatly affected by the presence of only a few alkali atoms on the surface [93,99,100]. In the case of potassium, as many as 25 CO molecules can be affected by long-range electrostatic interactions with one single potassium atom, that is, the effect of the K surface atoms extends as far as three lattice atoms away. On the other hand, there is a distinctly different short-range electrostatic effect in that system that affects only a small kernel of CO molecules next to the alkali. Theoretical calculations explain these two interactions by different perturbations of the valence charge density and the Fermi-level local density of states of the surface induced by adsorption. The left panels in Fig. 2 show that the electrostatic perturbation of sulfur atoms to the charge density of a Rh(100) surface is completely screened beyond the nearest-neighbor rhodium atoms around the S impurity [101,102]. This has been corroborated directly by STM measurements (Fig. 2, right) [103]. In contrast, the local density of states around the Fermi edge of the metal is modified upon adsorption over a wider lateral range, covering a radius of approximately three substrate atoms. This density of states is unscreened, and affects further chemisorption over large distances.

The idea of localized bonding applies to most surface systems studied to date, including small atoms and molecules such as hydrogen [104–106], nitrogen [107,108] and oxygen [88,109,110], oxides of carbon [111–115], nitrogen [94,116–124] and sulfur [125], hydrides such as ammonia [126–128], amines [129–131], phosphines [132–135], water [136,137], hydrogen sulfide [138–142] and hydrogen halides [131,143–145], a wide range of hydrocarbon molecules [79,146–148], including olefins [147–151], aromatics [152–158], cyclic hydrocarbons [159–163], alcohols [164–170] and other oxygenates [171–178], and other nitrogen- [130,158,179–183] and sulfur- [184–191] containing compounds. In most cases, molecular adsorption is characterized by the retention of the majority of the molecular orbitals and normal modes of vibrations, and by interaction with the surface via specific electron sharing with only one (or at the most a few) surface atoms. Adsorption studies have been predominantly carried out on transition-metal surfaces, where a large component of the adsorbate-surface chemistry can be described by bonding with the d orbitals of the metal. Less work has been done on more covalent compounds (oxides [192–197], carbides [198–202], nitrides [200,203]), but in those cases it has been shown that, if anything, the bonding of adsorbates is even more localized (because of the more

Surface Electron Density Changes Induced by Adsorption

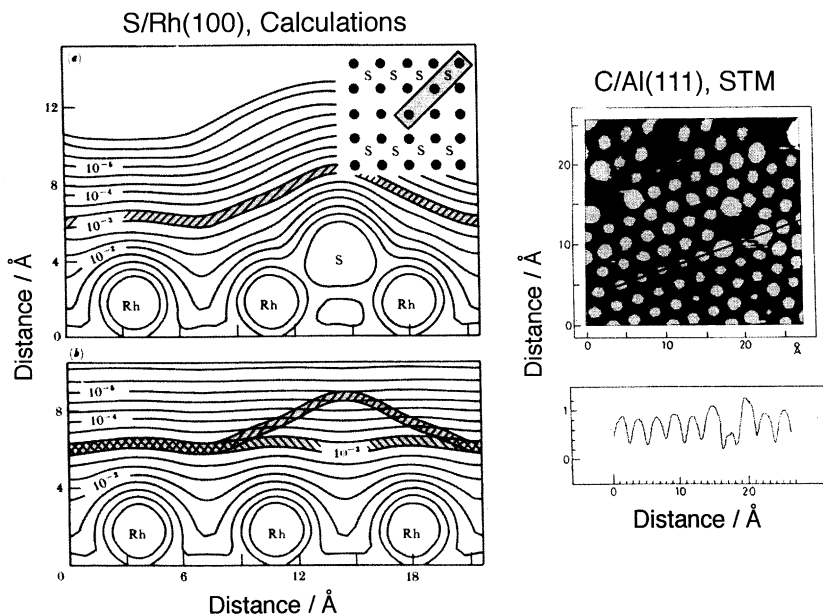


Fig. 2. Left: Theoretical calculations showing the variations in total valence charge density induced by adsorption of a sulfur atom on Rh(100) as a function of distance across and above the surface [101,102]. The calculation corresponds to a (3×1) S overlayer. Charge densities are shown as contour plots, in units of electrons/bohr³, and distances are provided in bohrs, 1 bohr = 0.529 Å. Right: STM experimental evidence for the variation in electron density caused by adsorbates. This example corresponds to the adsorption of carbon atoms on an Al(111) surface [103]. The dip in signal in the STM signal along the indicated $[1, -1, 0]$ direction corresponds to a carbon atom located in a threefold hollow site.

covalent nature of the bond). A wealth of “cluster” computational work to estimate adsorbate structures has relied on this idea of bond localization [204–208].

2.2. Adsorption geometries

A great deal of information has also been acquired on the geometry of adsorption of molecules on solid surfaces. Here, again, analogies with organometallic systems have been useful. The localized nature of the bonds has been corroborated by the particular atomic arrangement that adsorbates adopt with specific ensembles of surface atoms. For instance, the basic coordination geometries known for CO on metal complexes, namely, atop (linear), twofold bridged, and three- and four-fold nested, have all found their correspondence on surfaces [25]. In all those cases, it has been established that adsorption requires the molecular axis to be perpendicular to the surface, with the carbon end down closer to the surface [111,112]. Identification of those geometries has relied heavily on vibrational spectroscopies [209], but more direct methods such as LEED have also been widely employed for this endeavor

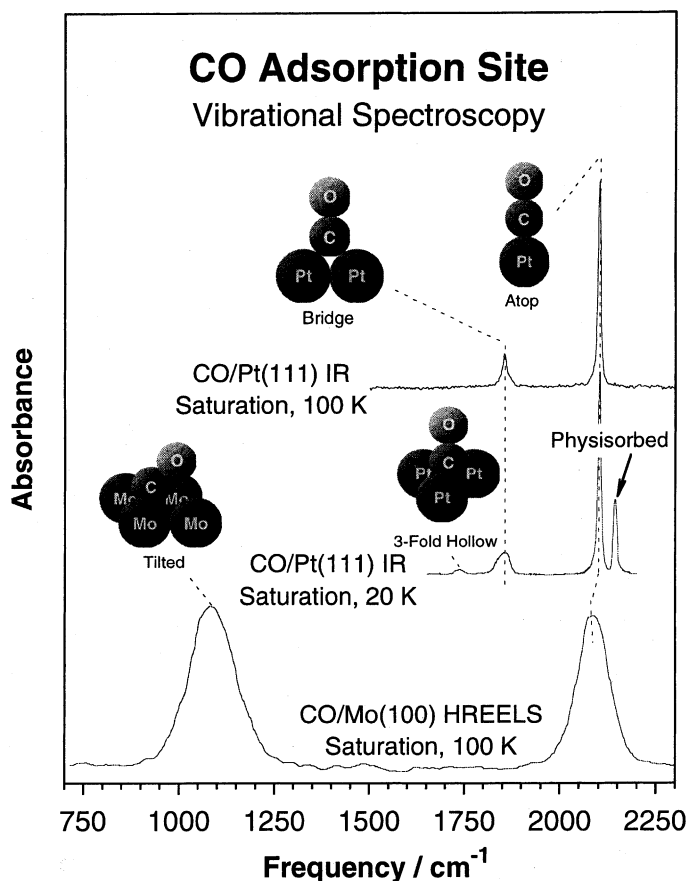


Fig. 3. Vibrational data for the C–O stretching mode in carbon monoxide adsorbed on transition-metal single-crystal surfaces. Highlighted here are the vibrational changes associated with changes in adsorption site. The top trace, which corresponds to a reflection–absorption infrared spectrum (RAIRS) obtained from a CO-saturated Pt(111) surface at 100 K, displays two peaks around 2100 and 1850 cm^{-1} for the atop and bridge adsorption geometries, respectively [377]. The middle trace was taken at 20 K, and shows two additional bands about 2145 and 1736 cm^{-1} , from physical and threefold hollow chemical adsorption, respectively [314]. The bottom data were obtained by using HREELS, and display a low (1235 cm^{-1}) frequency peak associated with the tilted adsorption mode of CO on Mo(100) [216].

[210]. Fig. 3 displays a couple of examples of vibrational data for CO adsorbed on Pt(111) single-crystal surfaces to illustrate how the rehybridization in the C–O bond induced by changes in adsorption local geometry can be used to determine the nature of the adsorption site [211]. A unique tilted CO adsorption geometry has also been observed in a few instances, concretely in the cases of Cr(110) [212,213], Fe(100) [214,215], and Mo(100) [83,216]; Fig. 3 reports the vibrational data for the molybdenum case. This tilted geometry is particularly interesting from the point of view of catalysis, because it displays both a low C–O stretching frequency and an un-

usually long C–O bond, suggesting that it could be the precursor to dissociation required in processes such as methanation and Fischer–Tropsch synthesis. Analogous examples of this geometry have been reported for discrete compounds as well [217,218].

A particularly interesting example of the success of using the surface–organometallic analogy in structural determinations on surfaces is that of the study of alkylidyne on transition metals [149]. It was long known that the thermal activation of ethylene on Pt(1 1 1) around room temperature yields a stable intermediate of C_2H_3 stoichiometry [219]. The identity of such moiety, however, remained controversial for some time. Ethylidene [220], vinyl [221], vinylidene [222], and ethylidyne [223] structures were all proposed. In the end, the latter prevailed, in great part thanks to a direct comparison with vibrational and structural data from an ethylidyne tricobalt nonacarbonyl compound [224]. Alkylidyne structures have since proven quite common [79], extending to longer hydrocarbon chains [151,225–229] and forming from a good number of hydrocarbon precursors [178,230–235] on a large number of metal surfaces [236–247]. Fig. 4 displays infrared and LEED structural data for ethylidyne and propylidyne on Pt(1 1 1) corroborating the proposed structure. These alkylidynes are believed to be quite important in hydrocarbon conversion catalysis [150,248–250].

Molecular geometries can be inferred directly from spectroscopic data [63]. Infrared [251,252], NEXAFS [57,58,253], and ARUPS [254–256] have, among others, been used extensively for this purpose. Although the use of spectroscopy for structural determinations often relies on previous knowledge on the electronic structure of the adsorbates, it has nevertheless shed much light on the nature of the interactions of molecules with surfaces. For one, it has helped determine that the geometry adopted by a chemisorbed moiety often changes in a dramatic way with the concentration of those species on the surface. 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 π 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) [154,155,257,258]. Reorientation induced by surface crowding has also been reported for alkyl [251,259] and alkoxide [260] groups. In addition, adsorption geometries may be affected by the structure of the surface. One dramatic example of this is that of ethylene on copper, where the flat geometry seen on most metals [79,147] is also observed on Cu(1 1 1) [261] and Cu(1 0 0) [262] but not on Cu(1 1 0) [263–265].

One of the most difficult aspects of structural studies on adsorbates is the determination of the details of the adsorbate–surface bond. Considerable progress has been made in this area, but a complete determination of chemisorption geometries using diffraction techniques has only been possible for relatively simple adsorbates [266]. Initial surface structural studies have relied on the use of LEED [87], have been limited by the required crystalline long range of ordered surfaces, and have often covered the structure of adsorbed atoms (O, S, K), diatomic (CO, NO, N_2 , O_2), or highly symmetric molecules (C_2H_2 , C_2H_4 , benzene). Fortunately, new developments

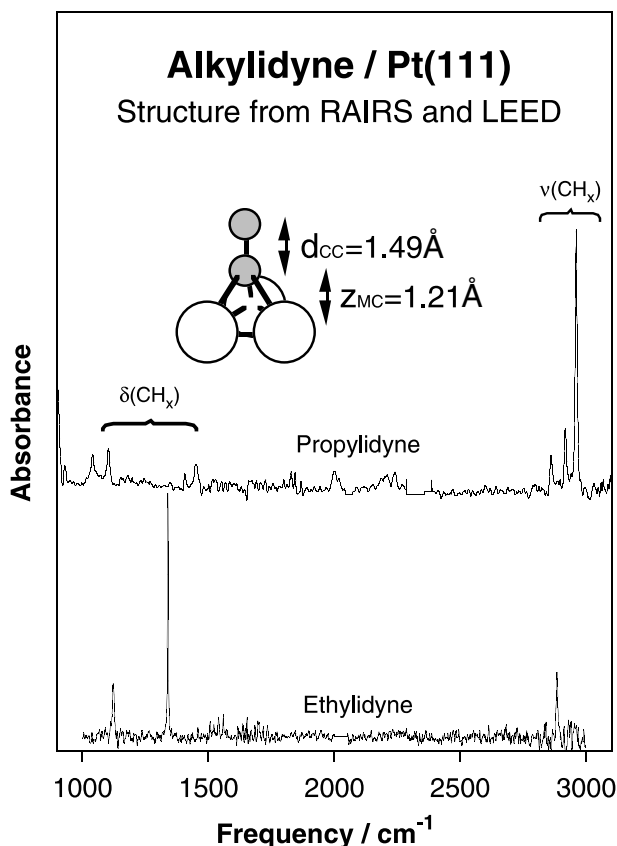
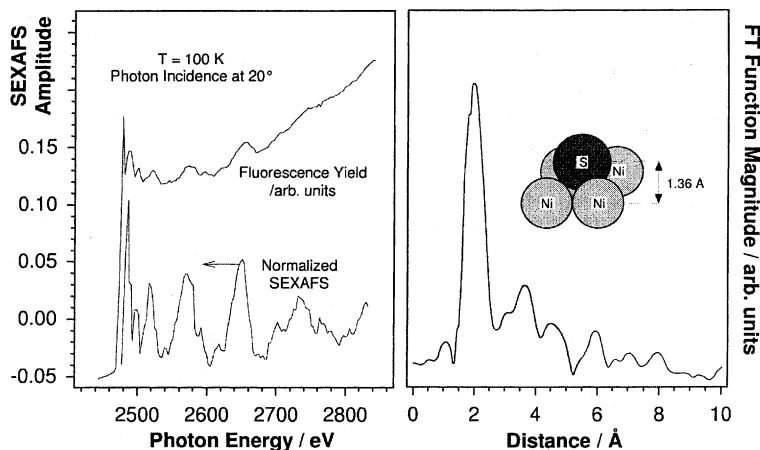


Fig. 4. RAIRS data for saturation layers of ethylidyne (bottom, [322]) and propylidyne (top, [229]) on Pt(111), prepared by room-temperature exposure of the surface to the corresponding olefin [788]. Also shown in this figure is the structure of the carbon backbone of ethylidyne, as determined by LEED experiments [931]. The C–C bond in that case stands perpendicular to the surface in the middle of a threefold hollow site, and is about 1.49 Å long (a distance typical of single bonds) and 1.21 Å above the surface plane. After some controversy, the final determination of these structures was finalized by comparison with infrared and X-ray crystallography data from a cobalt cluster analog [224].

are extending the use of LEED to larger systems [267] as well as to systems with no long-range order [268–271]. A number of additional techniques capable of probing local geometries have also been recently added to the tool box of surface chemists, including photoelectron diffraction (PED) [28], X-ray absorption spectroscopies (SEXAFS and NEXAFS) [57,58], and scanning microscopies [31]. There is now a reasonably large library of structures for adsorbed species [3], and some trends have become evident from those data. For instance, it is now known that most atomic species prefer to adsorb in nested geometries, and to bond to multiple surface atoms. An example of this is given in the top of Fig. 5, which shows the details of the fourfold coordination of sulfur atoms on Ni(100) determined by SEXAFS [272]. In

Sulfur Adsorbed on Ni(100) Structure Determination by SEXAFS



Chemisorbed Benzene on Rh(111) Structure Determination by LEED

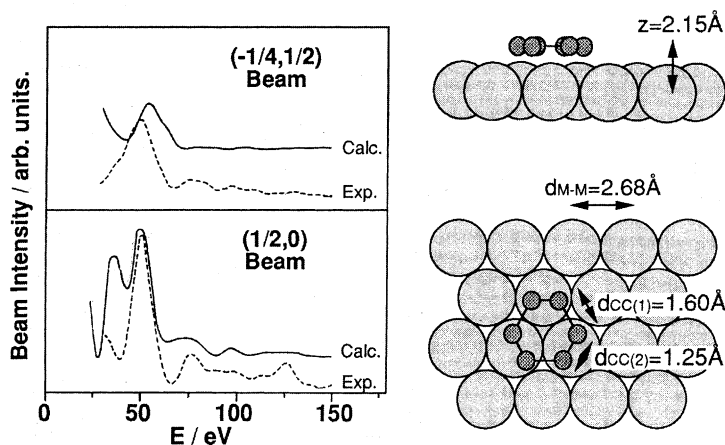


Fig. 5. Examples of structural determinations for adsorbates using interference and diffraction techniques. Top: Sulfur adsorption geometry on Ni(100), as determined by surface extended X-ray absorption fine structure (SEXAFS) spectroscopy [272]. The left panel shows both the raw data, as measured by following the intensity of the resulting X-ray fluorescence as a function of incident photon energy, and the normalized data. The right panel displays the radial distribution obtained by Fourier transformation of the normalized data, and a scheme of the proposed adsorption structure. Bottom: LEED determination of the adsorption configuration of benzene on Rh(111) [275]. In this case, not only was the position of the molecule with respect to the surface calculated, but also changes within the molecule were identified. Notice in particular the Kekulé distortion seen in the aromatic ring, where the C–C bonds rearrange to form a ring with alternating 1.25 and 1.60 Å bond lengths.

the case of unsaturated hydrocarbons, the molecules tend to coordinate with their plane parallel to the surface (at least at low coverages) in order to maximize the overlap of the π orbital(s) with the surface electronic states. As a result, some degree of rehybridization takes place. Olefins such as ethylene acquire more sp^3 character [149,237,273], and aromatic rings such as benzene buckle or become distorted [149,274]. The bottom of Fig. 5 provides an example for the latter, the LEED data used to determine the structure of benzene on Rh(111) surfaces [275]. Molecular distortions may be different on different surfaces: while alternating C–C bond distances are seen over the threefold hollow sites of Rh(111) surfaces [275], two opposite shorter bonds are observed in a bridge configuration on Pt(111) instead [276]. No clear explanation for this is yet available. Also unclear at present are the reasons for the changes in molecular coordination with respect to the surface atoms. For instance, while acetylene sits on a bridge site on Ni(111) [277], it does so in an atop configuration on Pt(111) [278]. The coordination of other hydrocarbons is even less defined at present. For example, there is still significant controversy on the adsorption site of alkyl moieties, with arguments been given for both atop [279,280] and nested [281] coordinations. Much remains to be done still in this area of structural determinations, especially with respect to complex and large molecules and surfaces.

Finally, additional consideration needs to be given to the potential rearrangement of surface atoms upon chemisorption. This is particularly important because solid interfaces have the tendency to reconstruct in order to minimize their surface energy [25]. In the case of metals, surface relaxation usually involves small atomic displacements, but in covalent compounds they often require the rearrangement of several layers: witness, for instance, the well-known (7×7) reconstruction of Si(111) [282], or the pyramidal reconstruction of polar surfaces such as NiO(111) [283]. The reconstructions of clean surfaces are usually removed upon adsorption, but sometimes at the expense of additional atomic rearrangements [284]. The most typical restructuring of metal surfaces induced by adsorbates is one where the first few planes expand or contract by up to 10% [285,286]. In other instances, lateral displacements of surface atoms [287], or even surface buckling [288], also take place. The high mobility of surface atoms induced by adsorbates has led to the suggestion that catalysts may be quite “flexible”, adapting the geometry of their surfaces during reaction to maximize their chemical activity [289]. However, this idea should be considered cautiously, because catalysts prepared in different ways often display significantly different activities [290–292], indicating that the original differences in structure resulting from those preparations cannot be completely erased by the adsorbates during the catalytic processes.

2.3. *Adsorption energetics*

One issue closely related to the nature of the surface bond is that of its energy. Bond energies between adsorbates and surfaces have traditionally been estimated from heat of adsorption data, as extracted from adsorption isotherms [1]. Fig. 6 displays the heats of adsorption for oxygen, carbon monoxide, and hydrogen across

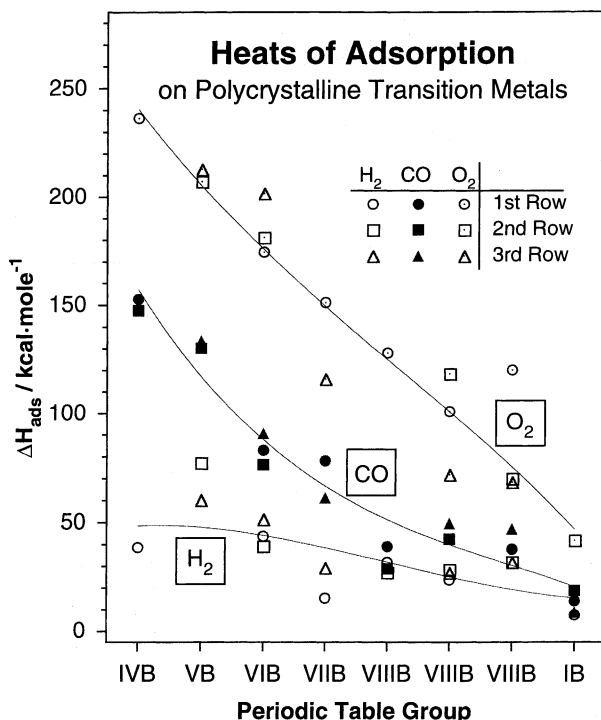


Fig. 6. Heats of adsorption for hydrogen, carbon monoxide, and oxygen on polycrystalline surfaces of transition metals [25]. A general trend is seen in all cases, the adsorption energies decreasing from left to right of the periodic table. In contrast, no significant differences are seen between first-, second-, and third-row metals. It has also been observed that adsorption energies on polycrystalline surfaces are significantly higher than on the most stable planes – (111), (100), (110) – of single crystals, perhaps because of the stronger interaction of adsorbates with surface defects.

the transition-metal segment of the periodic table [25]. One clear trend from those data is the fact that adsorption energies usually decrease from left to right in the periodic table. Put another way, early transition metals typically display more aggressive chemistry than late ones. Notice that the adsorption of both oxygen and hydrogen is dissociative, and that the end state in those cases is two atoms bonded to two adsorption sites. Taking this into account, bond energies can be easily calculated from adsorption data. For hydrogen, they go from about 90 kcal/mol on Ta and Nb, to around 55 kcal/mol on Cu, while for oxygen the range is from 180 to 80 kcal/mol. It is also worth mentioning that there is a good correlation between the heats of adsorption of oxygen on transition-metal surfaces and the heats of formation of the corresponding metal oxides [88]. This indicates that the surface bond is essentially similar to those in bulk compounds.

Unfortunately, most heat of adsorption measurements reported to date have been carried out on supported catalysts, and therefore only correspond to average values. It has been long recognized that adsorption energies depend strongly on the local

structure of the surface, something difficult to control during catalyst preparation. Studies of heats of adsorption on single-crystal surfaces have indeed corroborated the differences in adsorption energies associated with the different surface planes of a metal [25]. For instance, the heat of adsorption of O_2 goes from about 140 kcal/mol on W(1 0 0) to about 160 kcal/mol on W(1 1 0) [293]. These numbers need to be taken with some reservation, however, because big differences are also encountered among different studies of the same system: reported values for the adsorption energy of oxygen on W(1 0 0) vary all the way from less than 100 to over 170 kcal/mol [25]. One safe conclusion drawn from adsorption energy data is that bonding on basal planes is significantly weaker than on polycrystalline samples: the value for O_2 adsorption on polycrystalline tungsten, for example, is about 200 kcal/mol. This is presumably due to the fact that adsorption is in most cases significantly stronger on surface defects such as steps and kinks, that is, on metal atoms with lower coordination numbers [294,295].

Adsorption energies depend on surface coverages as well. This is to be expected, given the spatial extent of the changes in surface electronic structure induced by the adsorbates (see Section 2.1), and has been observed directly in experiments with single crystals. For instance, the heat of adsorption of CO on Pd(1 1 1) starts about 35 kcal/mol on the clean surface, but decreases to less than 30 kcal/mol by the time a coverage of half a monolayer is reached [296]. It has been empirically determined that adsorption energies often vary in an approximately linear manner with coverage. The left panel of Fig. 7 illustrates this for the case of the adsorption energies of ammonia on Cu(1 0 0) [297]. Such behavior has been accounted for by a number of models based on adsorbate–adsorbate pairwise interactions [298,299]. On the other hand, abrupt drops in adsorption energy are commonly observed beyond a critical coverage (usually corresponding to an ordered overlayer). This is typically associated with the formation of “compressed” layers. In the case of CO/Pd(1 1 1), additional molecules can be added to the surface beyond half a monolayer (which displays a $c(4 \times 2)R45^\circ$ structure), all the way to about 80% of a monolayer, but only after a sudden drop in adsorption energy to below 20 kcal/mol [296].

Most of the adsorption energy data available on single-crystal surfaces to date have been acquired by temperature-programmed desorption (TPD) experiments. TPD is a powerful technique that provides large amounts of kinetic and stoichiometric information from a few simple experiments [69,70]. It does, however, suffer from a number of drawbacks. For one, TPD measures activation energies; heats of adsorption can be estimated from those only by assuming non-activated adsorption. More importantly, that technique measures desorption rates as the temperature of the surface is ramped, and under those conditions surface temperature and surface coverages change simultaneously and in a correlated fashion. A number of mathematical treatments have been developed to extract kinetic parameters from such data [300–304], but, ultimately, TPD is not very sensitive to the independent contributions of coverage-dependent preexponential factors and activation energies to the overall kinetics of desorption.

There have been some recent advances in the determination of adsorption energies isothermally on single-crystal surfaces. In reversible cases, where an equilibrium

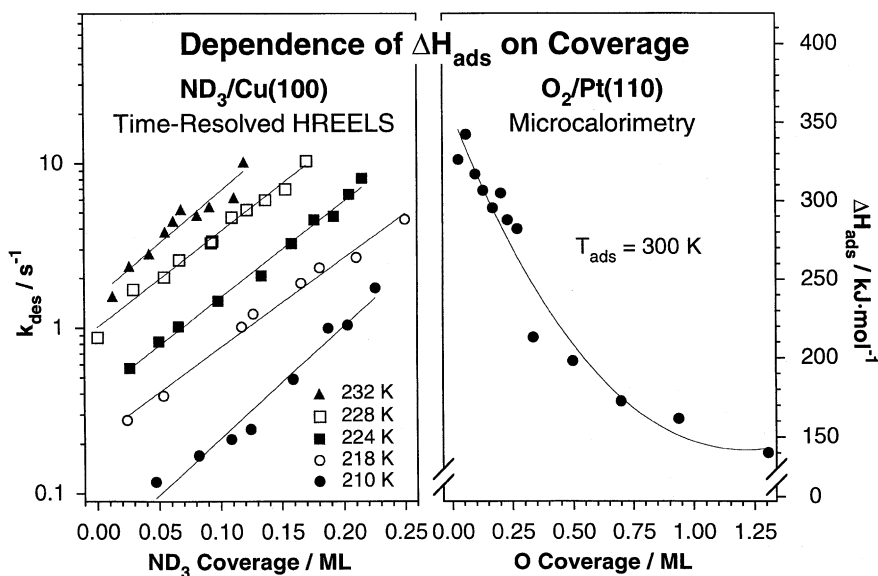


Fig. 7. Examples of the dependence of adsorption energies on surface coverages. Left: Desorption isotherms for deuterated ammonia from Cu(100), as followed by time-resolved HREELS [297]. The linear dependence of desorption reaction rate constants on coverage in this semilogarithmic plot argues for a similar linear dependence of activation energies of desorption on coverage. Right: Differential heats of adsorption for oxygen on Pt(110) at 300 K as a function of coverage, as measured by microcalorimetry [309]. In both cases, the adsorption energy decreases with coverage, an indication of overall adsorbate–adsorbate repulsive interactions.

between the surface and the gas phase can be established, molecular beams can be used to perform experiments not only isothermally but also at constant coverage [305,306]. A wealth of information can be obtained that way. In particular, it has been found that activation energies are in fact not linearly dependent on coverage, as mentioned previously [305]. A theoretical model where the rate of desorption is expressed in terms of chemical potentials and where the chemical potentials are written in a Virial expansion accounts for such deviations [307]. In another development, it is now possible to measure heats of reactions on single-crystal surfaces directly via the use of a newly designed microcalorimeter [308]. Again, strong non-linearities between adsorption energies and coverages have been measured this way. The data reported in the right panel of Fig. 7 for oxygen adsorption on Pt(110) illustrate the point [309].

Finally, much less is known about the binding energy of species that cannot be directly dosed from the gas phase or do not desorb molecularly from the surface. One way energies have been estimated for those systems is by constructing a Hess cycle around a set of reactions for which activation energies are known in both directions. A fine example of this is illustrated by the data in Fig. 8, which correspond to the formation of ethyl groups on Pt(111) [310]. Bond energies for metal–carbon bonds are now available for methyl and ethyl groups on nickel, platinum, copper,

Surface Bond Energy From Hess Cycle

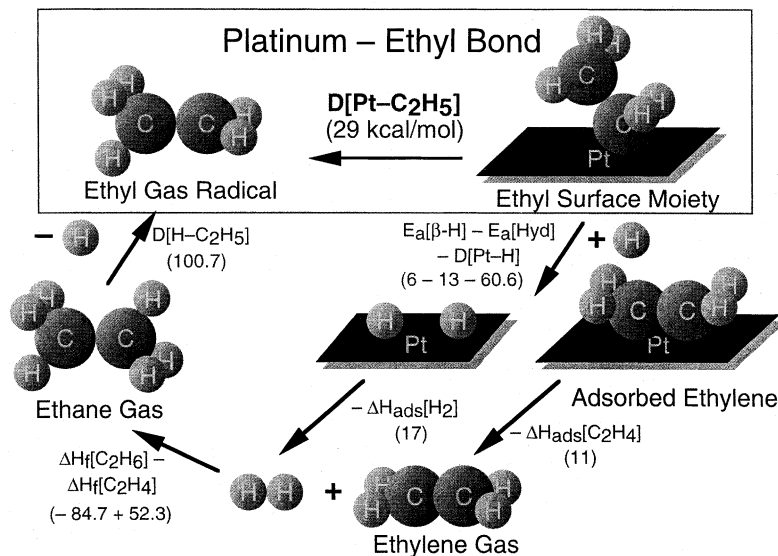


Fig. 8. Hess cycle of the kind used to estimate surface bond energies. In this case, the dissociation energy of the bond between Pt(111) atoms and ethyl moieties is calculated by using the activation energies for β -hydride elimination, ethyl-hydrogen reductive elimination, and hydrogen and ethylene desorption steps, all measured by TPD, as well as the reported heats of formation for ethylene and ethane and the C–H bond energy in ethane [310].

and iron surfaces: they all display values of about 30–35 kcal/mol, irrespective of the metal or the crystallographic plane of the surface [79,146]. In cases where the surface reaction being considered is a clean elementary step, microcalorimetric measurements can also be carried out to determine the heat of reaction directly [311].

2.4. Production of unstable surface intermediates

Most of the examples mentioned so far refer to species adsorbed on surfaces directly from the gas phase. There are, however, a large number of unstable surface intermediates believed to be important in catalysis which cannot be isolated that way. In particular, catalysis often relies on weakly adsorbed or transient species with short lifetimes; a steady-state concentration of those can be maintained only because of the continuous replenishing of adsorbates with molecules from atmospheric-pressure gases. This situation is not easy to reproduce in modern surface-science studies, where ultrahigh vacuum is required. In simple cases the problem generated by the use of lower pressures can be compensated by also lowering the surface temperature. This approach has been used to isolate and characterize a number of surface precursors, including molecular oxygen (in its way to dissociation into ox-

xygen atoms) [312] and π -bonded olefin (which then rehybridize into a di- σ coordination) [313]. It has also allowed for the freezing of adsorbates in unstable adsorption sites, as in the case of CO coordination to threefold hollow sites [314], and for the exploration of surface diffusion.

A number of alternative procedures for the preparation of surface intermediates has been developed over the years as well [146,231]. Fig. 9 depicts schematically some of those methods for the case of surface methyl production. In many instances, surface intermediates can be produced cleanly via thermal activation of other adsorbates. This procedure works well when surface elementary steps can be identified and isolated. For example, many atomic species can be produced by dissociation of diatomic molecules: witness the extensive use of H_2 [104,106] and O_2 [88,90,110] to produce atomic H and O on surfaces, respectively. Also common is the removal of labile hydrogen atoms for the production of specific hydrocarbon moieties. Extensive work has been done, for instance, on the characterization of alkoxides and carboxylates, which can be produced via thermal activation of the appropriate alcohols and organic acids, respectively [171,315–317]. A similar approach has been used for the study of thiolates starting from thiols [188,318]. Cyano groups have been prepared using HCN [319–321], although an alternative and perhaps cleaner route in that case is to start with C_2N_2 [127]. Dehydrogenation, together with isomerization, leads to the clean formation of alkylidyne species from adsorbed olefins, as men-

Surface Alkyl Preparation Methods

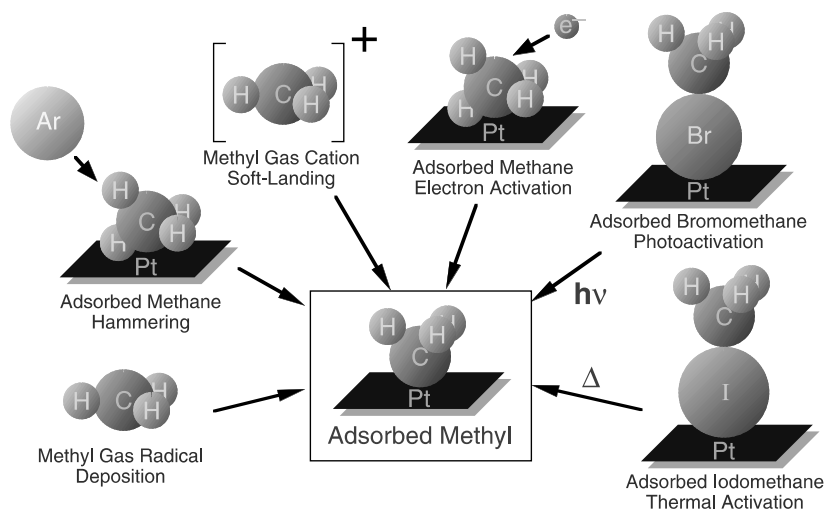


Fig. 9. Schematic representation of some of the methods reported in the literature for the preparation of methyl surface groups on solid surfaces [79,146,231]. From left to right: deposition of gas methyl radicals prepared by azomethane pyrolysis [362], activation of adsorbed methane by hyperthermal atoms [373], soft-landing of gas-phase methyl cations [367], electron activation of adsorbed methane [369], photoactivation of adsorbed methyl bromide [368], and thermal activation of methyl iodide [736,750].

tioned above [225,322]. Intermediates can also be produced by association of reactants on the surface. This is much more difficult to achieve, but has nevertheless been employed for the production of ethyl species on copper either via addition of gas-phase hydrogen [323] or by methylene insertion into a metal–methyl bond [324].

A related approach for the preparation of specific surface intermediates is to start with appropriate precursors with a specific weak bond. For instance, fluorine atoms can be produced cleanly by thermal activation of adsorbed XeF_2 [325]. High coverages of atomic oxygen can be deposited by strong oxidants such as NO_2 or ozone [326]. Perhaps the most widespread use of this idea in recent times has been in the preparation of hydrocarbon surface moieties using halohydrocarbons [146,231,327–329]. Alkyl moieties, in particular, have been studied on many surfaces this way [170,330–335], as in the case of methyl production from methyl iodide indicated in Fig. 9. Extensions of the use of such halides to the production of carbenes [335–338], vinyls [234,235], allyls [162,339–341], metallacycles [342–346], and oxametallacycles [347,348] have been reported as well. It should be pointed out that the success of this approach is by no means guaranteed. For instance, in spite of the low binding energy of the C–N bonds in azo and diazo compounds, those adsorbates display fairly complex surface chemistry: no clean production of alkyl groups has been possible with chemisorbed azoalkanes [183,349]. The use of ketenes [350] and peroxides [351], well-known precursors for the production of free radicals [352], has barely been explored to date for the deposition of surface species.

One difficulty with the use of precursors for the production of adsorbed intermediates is that they codeposit other species (the halogen atom in the case of halohydrocarbons) on the surface. One way around this problem is to use organometallic compounds, preferably those containing the metal of the substrate and the ligand of interest. This approach has severe limitations, since it requires the availability of very specific metal complexes, and can also lead to a rougher surface, but has been employed successfully in the cases of trialkyl aluminum on $\text{Al}(1\ 1\ 1)$ and $\text{Al}(1\ 0\ 0)$ [353], diolefin dialkylplatinum(II) on platinum films [354], trialkyl bismuth on $\text{Pt}(1\ 1\ 1)$ [355], and diethyl zinc on $\text{Pd}(1\ 0\ 0)$ and $\text{Rh}(1\ 1\ 1)$ [356].

When molecular species cannot be isolated cleanly on surfaces, they may be prepared in the gas phase and then dosed on the substrate. This is particularly feasible with free radicals for which synthetic routes are already known. The simplest example of this in surface studies is the production of atomic hydrogen via the pyrolytic decomposition of H_2 gas [357]. Similar sources have also been developed for the production of oxygen [357] and halogen [358] atomic beams. Sulfur and selenium [359,360], and fluorine, chlorine and iodine [361] atoms can also be produced by using solid-state electrochemical cells.

Unfortunately, the clean production of molecular fragments is a much more difficult task. Methyl groups can be deposited from the gas phase after pyrolysis of azomethane (Fig. 9) [362], but it has not been possible to generalize this procedure to other alkyl groups. Some radicals have been produced and state-selected via hexapole filtering of radicals from a plasma discharge and deposited on $\text{Pt}(1\ 1\ 1)$ surfaces, including OH, [363] CF_x , SiF_x , SH, and CH species [364]. In addition, CO^+ [365], H_3O^+ [366], and CH_3^+ [367] ions have all successfully been produced and soft-landed

after deceleration to kinetic energies of only a few eV on solid surfaces (the case of CH_3^+ is also included in Fig. 9). However, these molecular radical and ion filtering experiments are all quite difficult, and are not easy to generalize.

Finally, surface intermediates may be created via manipulation of adsorbed species by means other than thermal activation. Electron-induced dissociation of adsorbed molecules can in many instances generate unstable surface species [368]. When applied to hydrocarbons, only one C–H bond is often broken in the process [369]. The reaction between adsorbates and electrons may be non-selective, but may yield a single intermediate when the precursor is a highly symmetric molecule. Surface methyl (Fig. 9), cyclopropyl, cyclohexyl, vinyl, and benzyl moieties have been prepared via electron-induced dissociation of methane, cyclopropane, cyclohexane, ethylene, and benzene, respectively [369]. Photon excitation can also be used to activate weak surface bonds, typically via the photoinduced transfer of electrons from the surface to the adsorbate [370–372]. The use of this method in systems of catalytic interest has so far focused mainly on the activation of halohydrocarbons (Fig. 9). Lastly, there has been, to the best of our knowledge, only one report of surface intermediate synthesis via activation of adsorbates by collision with hyper-thermal gas molecules, that of methyl formation from methane on Ni(1 1 1) (Fig. 9) [373]. This is an extremely difficult experiment to perform, and can lead to unpredictable results.

3. Surface kinetics

As mentioned in the previous section, a large amount of effort within the surface-science community has been spent on the isolation and characterization of surface species of potential relevance to catalysis. An almost equal level of research activity has been directed towards studying the thermal chemistry of those intermediates. However, the bulk of the experiments in this direction has been limited to the identification of decomposition pathways, and even there, only the first steps of those reactions have been identified. The systems characterized by these studies include bond dissociation of simple (H_2 , O_2 , NO, CO, HCN, etc.) molecules, dehydrogenation (and sometimes hydrogenation) of olefins and other hydrocarbons [149,150], conversion of alcohols and other oxygenates [171], amines and other nitrogen-containing molecules [158,183], and thiols [318], and oxidation of carbon and nitrogen oxides [374–377] and of hydrocarbons [170,378–380]. Reference to some of those reactions will be made throughout the rest of our review as examples are required. What has often been missing is a careful determination of the kinetics of the surface reactions. Issues related to chemical kinetics will be addressed next.

3.1. Adsorption

Much of our understanding on the kinetics of adsorption has been obtained from molecular beam studies (see Section 4.1) [381,382], although many spectroscopic methods have also been used to follow the uptake of gases on surfaces. From the

kinetic point of view, adsorption is described in terms of sticking coefficients, that is, in terms of the probability that molecules impinging on a surface adsorb instead of scatter back into the gas phase. Initial sticking coefficients (s_0) on clean surfaces are often quite high on metals, close to unity, as in the cases of H_2 [383–387], O_2 [388–390], N_2 [391,392], CO [393–398], CO_2 [399], NO [123,400–403], NO_2 [404], SO_2 [405], H_2O [136], NH_3 [406,407], olefins [408,409], alcohols [410], and other hydrocarbons [411], but they can also be very low (10^{-10} or lower), in particular with saturated hydrocarbons [412–415]. The values for s_0 on oxides [110,197,416] and other covalent solids [203] are also typically much lower. Chemisorption can be molecular, as is often the case with CO , NO and olefins, at least at low temperatures, or dissociative, as, for instance, with H_2 and alkanes. The probability for adsorption depends only weakly on temperature, that is, adsorption is quite often unactivated (see later), although in some cases (H_2 on copper [417], for instance) small activation barriers have been measured.

Sticking probabilities change significantly with coverage, primarily because of the filling up of adsorption sites on the surface. Langmuir developed a simple model in 1918 to describe such behavior based on geometrical arguments in which the probability for molecular adsorption decreases linearly with coverage [418]. That model, later extended to include dissociative adsorption, has been successful in describing many adsorption systems [419]. More often, however, sticking coefficients remain quite high even when the surface is partially covered with adsorbates [397]. This has been explained in terms of weakly adsorbed and mobile precursors. The idea is that when molecules from the gas phase impinge on occupied adsorption sites, they may be trapped in a physisorbed state, and diffuse along the surface until they find an available empty site. A number of theories have been developed to incorporate this concept [420–422], the most popular being the one put forward by Kisliuk [423]. A distinction is made in some of those models between intrinsic and extrinsic precursors: a precursor is considered intrinsic if it is trapped in a shallow well in the potential energy surface of the clean surface, but extrinsic if the physisorbed state is located on top of another chemisorbed molecule.

The kinetics of adsorption can be further complicated by the dependence of adsorption energies on coverages. This can be due to a number of reasons. For one, different adsorption sites with different adsorption energies may be present on the surface, and adsorption may then take place so those get filled sequentially. This is particularly plausible in heterogeneous supported catalysts, where the structure of the surface is ill defined [1]. Adsorption at steps and other surface defects has in fact been shown to display significantly different energetics [377,424]. Alternatively, the changes in adsorption energy may be due to the collective effect of increasing adsorbate–adsorbate interactions with increasing coverages. Isotopic labeling experiments have shown that this is often the case on single-crystal surfaces [409,425]. Finally, both surface diffusion of adsorbates and island formation can also alter the kinetics of adsorption [426,427].

Thanks to the development of the so-called King and Wells beam technique [397,428,429], good data are now available on the coverage dependence of sticking coefficients for many systems, in particular on single-crystal surfaces. As a result,

some subtleties not previously noticed have been identified. There are many sets of experimental data on adsorption kinetics that cannot yet be completely described by the models mentioned above, so more work is still needed in this area. The time is also ripe for the characterization of adsorption under competitive conditions among two or more gases. One interesting observation is that some gases are capable of displacing other adsorbates from the surface. Tamaru [430] originally baptized the displacement of adsorbed CO by other incoming CO molecules as “adsorption-assisted desorption”. Muetterties et al. [431] exploited analogies with organometallic systems to propose the displacement of some adsorbates (such as benzene) by others (such as phosphines). NO has been shown recently to displace adsorbed CO on Rh(111) [432]. In all those cases, the displacing molecules bind more strongly to the surface than the ones being displaced. In addition, synchrotron and isotope-labeling TPD studies on Ni(100) indicated that it is even possible to displace CO by more weakly adsorbed hydrogen molecules [433]. Further studies on the CO/Ni(100) and CO/Pt(111) systems with He, Ne, Ar, N₂, H₂ and D₂ suggested that this CO displacement does not result from a direct dynamic effect exerted by the gas-phase molecules, but rather it is the consequence of CO adsorption weakening by the coadsorbed hydrogen [434].

The displacement of adsorbates by fresh gas-phase molecules impinging on the surface has some important implications for the overall kinetics of catalysis. This is because the effective sticking coefficient of a given reactant can change when in gas mixtures with other gases. For instance, the initial sticking coefficients of NO and CO on Rh(111) have been reported to vary by as much as an order of magnitude depending on the NO:CO ratio in the gas mixture [432], and the steady-state rate of the NO catalytic reduction by CO appears to correlate reasonably well with those changes (Fig. 10). Very little work has been done to date to explore this issue in detail.

3.2. Desorption

As mentioned in Section 2.3, most of the desorption kinetic data available on single-crystal surfaces to date come from TPD experiments [69,70]. In fact, TPD is a kinetic experiment; heats of adsorption are obtained from it only by assuming that the reverse adsorption is non-activated. Thanks to TPD, a large database of activation energies for the desorption of simple molecules from single-crystal metal surfaces can be found in the literature. Nevertheless, all the limitations of TPD mentioned before apply to the determination of desorption kinetic parameters as well. In particular, because reaction rates are measured as both temperature and surface coverage are simultaneously changed, it is difficult to separate the contributions of changing coverages to each of the main kinetic parameters (reaction order, activation energy, and preexponential factor). This is critical, because, as with adsorption energies, activation energies are often not constant, but depend on coverage. For instance, first-order desorption processes should display TPD traces with maxima at the same temperature regardless of initial coverage, but this is in most cases not what is seen [435]. Such deviations have been explained by an increase in adsorbate–adsorbate interactions with increasing coverage.

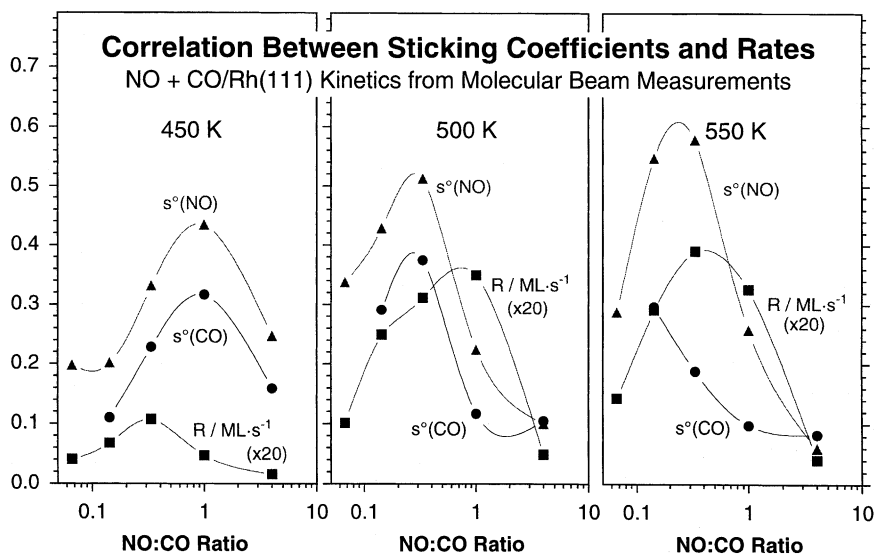


Fig. 10. Correlation between sticking coefficients and steady-state reaction rates for the conversion of carbon monoxide and nitrogen monoxide mixtures to molecular nitrogen and carbon dioxide on Rh(111) [432]. The data, obtained by using a molecular beam, correspond to three surface temperatures, 450, 500, and 550 K. Similar, although not identical, trends are seen for the adsorption probabilities of both CO and NO and for the reaction rates with varying gas mixture composition and temperature. It is worth noting that the sticking coefficients reported here are associated with competitive adsorption conditions, with both CO and NO molecules impinging simultaneously on the surface.

The problems with the analysis of TPD data when kinetic parameters depend on surface coverages, as they often do, are quite general. An extreme case of this is that of benzene on Pd(111), where two TPD peaks are observed at quite different temperatures [436]. It is believed that the initial saturation layer in that system is composed of tilted benzene held relatively weakly on the surface, but that, as desorption occurs, a critical coverage is reached where the aromatic rings reorient to a geometry parallel to the surface plane, increasing the adsorption energy in a significant way. An additional question arises in connection with the formation of compressed layers: are all molecules equivalent in that state, or are there two or more distinct adsorption states which fill in sequentially on the surface? Different answers to this question have been obtained depending on the system addressed. For instance, weakly and strongly adsorbed ethylene molecules on Pt(111) can be easily exchanged, as indicated by isotope-labeling experiments, suggesting that they all change adsorption sites collectively [409]. A more complex behavior is seen with CO on Fe(100), where no conversion occurs between the α - and β -CO or between the α_1 and α_2 CO states, but where significant conversion is observed between the α_2 and α_3 states [437]. A number of kinetic models and computer simulations have been developed to address these problems [301,302,304,438], but none have been able to completely overcome the intrinsic limitations of TPD. Ideally, desorption

experiments need to be carried out isothermally. Unfortunately, that adds a significant level of experimental difficulty. To the best of our knowledge, isothermal desorption experiments with mass spectrometry detection have only been reported for the case of CO on Ni(110) [439].

One final complication in determining desorption kinetic parameters worth mentioning here is surface diffusion. In bimolecular reactions in particular, that is, for recombinative desorption, the relative rate of diffusion of the recombining fragments determines the apparent order of the kinetics of desorption observed. This is the reason why, even though it is well known that oxygen adsorbs in atomic form on most metal surfaces, first-order desorption kinetics is often observed for those systems [404]. When surface diffusion is limited, only recombination among neighboring atoms is possible, so the bimolecular step appears to be unimolecular as far as its kinetic behavior is concerned. In a similar fashion, molecular desorption can sometimes display zero-order kinetics. In that case, it is possible for desorption to take place from only a few special sites (steps etc.) on the surface: if diffusion of the adsorbates is rapid, the total desorption rate is controlled by the concentration of those desorption sites on the surface [440–442].

3.3. *Surface diffusion*

As mentioned above, diffusion of adsorbed species across the surface can influence the overall kinetics of adsorption, desorption, and surface reaction steps. Rates and kinetics parameters for surface diffusion have been determined by a number of techniques, mainly for atoms, but also for some diatomics [443]. Overall surface diffusivities have been studied mostly by measuring mass transport across clean surfaces. One approach has been to follow the temporal behavior of the refilling of a surface area cleaned by laser-induced desorption [444,445]. At the other end, several microscopies, including field ion [446,447], field emission [448], and scanning tunneling microscopies [449–452], have been used to characterize the migration of individual atoms on surfaces. A few general observations have come from that work.

The diffusion process can be described as the motion of the adsorbates across a corrugated potential with energy wells at the lattice points where the most stable adsorption sites are. The height of the energy barriers is directly related to the binding energy of the adsorbate, amounting to somewhere between 5% and 20% of the desorption energy in close-packed flat metal surfaces [453]. The diffusion kinetics can be described by Fick's law of diffusion, although a distinction needs to be made between atomic diffusion constants, D_a , as calculated from the average motion of single isolated adsorbates, and chemical diffusion constants, D_c , which refers to the total flux of particles; the two agree only when the motion of the different adsorbates are uncorrelated (usually not the case, see below) [454]. The preexponential factor of surface diffusion constants, D_0 , is often of the order of 10^{-3} cm²/s, as expected for a frequency factor of 10^{13} s⁻¹ at the bottom of the chemisorption potential well [455]. Diffusion typically occurs by single hops between adjacent potential wells, although multiple site jumping does occur on occasion [456].

It has also been shown that in non-symmetrical surfaces there can be some diffusion anisotropy. In particular, steps have been shown to inhibit diffusion. Accordingly, on stepped surfaces, diffusion in the direction parallel to the steps can be several orders of magnitude faster than that across the steps [457–459]. Moreover, since adsorption is usually stronger at surface defects, atoms and molecules may diffuse and become trapped at those sites. Typically, adsorption takes place at the bottom of steps; the barrier to the ledge of those steps is often insurmountable at reasonable temperatures. Finally, dimers and bigger clusters of adsorbates may diffuse at faster rates than individual atoms, presumably because of a cooperative motion in which lateral interactions help overcome the activation barrier for diffusion [460,461]. Fig. 11 shows a nice recent example of this, an STM picture highlighting the collective motion of CO adsorbate chains on Cu(1 1 0) [462].

Role of Adsorbate Interactions in Surface Molecular Diffusion

CO/Cu(110) STM, 44 K

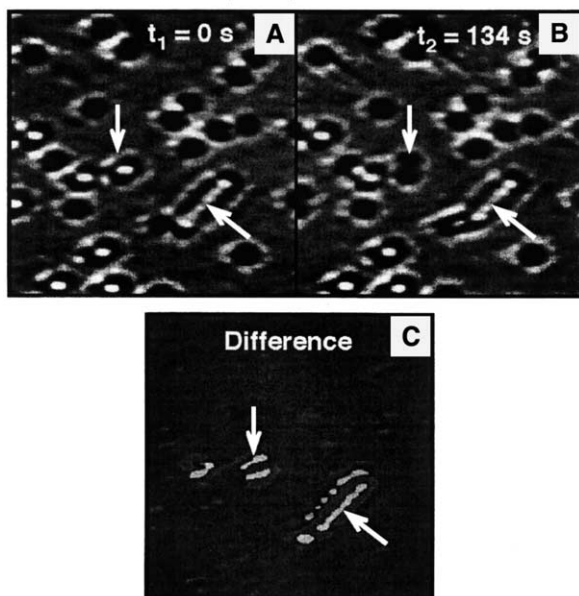


Fig. 11. STM images illustrating the collective motion of adsorbates when diffusing on solid surfaces. This example corresponds to the displacement of carbon monoxide molecules on a Cu(1 1 0) surface at 44 K [462]. The two top images correspond to the same section of the CO/Cu(1 1 0) surface, only taken 134 s apart. The bottom panel displays the difference between the two, and highlights the changes due to surface diffusion. The arrows point to the lateral motion of some of the CO chains, seven molecules long in the case of the cluster on the right. Surface diffusion is often aided by the presence of other adsorbates in neighboring positions.

3.4. Surface reaction steps

Studies on the kinetics of surface reaction steps have been carried out mostly by TPD. If desorbing products other than the original adsorbates are detected by mass spectrometry, the inference is made that a surface reaction has taken place. At that point, it needs to be determined if the observed process is an elementary step or the consequence of a complex set of reactions. That is sometimes easy to establish (depending on the nature of the reactants and the products), but typically requires additional spectroscopic evidence. An additional assessment of the rate-limiting process is also often needed, usually the surface reaction or the desorption of the products. After all those questions have been answered in a positive way, some useful kinetic information may be extracted from the thermal desorption data.

One family of reactions where this application has been of some use is the dehydrogenation of hydrocarbons. Desorption of the resulting hydrogen can be said to be reaction-limited if detected at temperatures above those needed for the recombinative desorption of atomic hydrogen, which on most transition metals occurs around or below room temperature. For instance, the desorption of H_2 from dehydrogenation of 2-propoxide intermediates on Ni(1 0 0) peaks around 320 K, and is accompanied by the desorption of one of the main products, acetone [334]. Since molecular acetone desorbs from Ni(1 0 0) at about 140 K, the TPD signal seen at 320 K when starting with 2-propanol is clearly reaction-rate limited. In that example, it was possible to extract additional kinetic information, because it is well known that alcohols dehydrogenate to form alkoxides at low temperatures, so it could be established that 2-propoxide is the reactant for the dehydrogenation step observed, a fact corroborated by infrared spectroscopy [463]. Additional isotopic labeling experiments proved the regioselectivity of the dehydrogenation step at the beta position, and strongly suggested the elementary nature of this reaction step [334]. Once all the information was put together, it could be established that β -hydride elimination from 2-propoxide species adsorbed on Ni(1 0 0) to produce acetone is associated with an activation barrier of about 20 kcal/mol.

Things do not always work out as nicely as in the example cited above. For one, many dehydrogenation steps are fast, and take place at lower temperatures than those needed for hydrogen desorption. If this is the case, the H_2 TPD traces are of no use for the determination of reaction kinetics. β -Hydride elimination from alkyl groups on late transition metals falls into this category [328,464]. Alternatively, hydrogen recombination may compete with hydrocarbon dehydrogenation, in which case TPD traces reflect the complex kinetic behavior resulting from combining the two reactions. The dehydrogenation of ethylene to ethylidyne on Pt(1 1 1) provides an example of this [465]. Finally, dehydrogenation may take place at high temperatures, but in a rapid sequence of non-separable steps. That is the case in the decomposition of alkylidynes [219,466], and also in the hydrogenolysis of neopentyl groups to isobutene on Ni(1 0 0), which isotopic labeling experiments suggest takes place by the concerted removal of two hydrogen atoms (at the alpha and gamma positions) and the scission of the C_α – C_β bond [467]. The overall activation barrier for

the latter step was estimated at ~ 25 kcal/mol. A recent study with neopentyl thiol on Fe(1 0 0) displays similar chemistry [468].

Another common reaction observed on single crystals under vacuum is the decarbonylation of oxygenated compounds such as alcohols, aldehydes, ketones, and organic acids [167,170,171]. Unfortunately, those processes are typically fairly complex, and are not easy to dissect into their constituent elementary steps. An extreme of this is the case of unsaturated aldehydes on platinum, acrolein and crotonaldehyde in particular, which appear to decompose via bimolecular reactions [178]. As long as no elementary steps can be identified, the apparent activation energies estimated by TPD cannot be associated with specific surface reactions. Additional complications appear when dealing with bimolecular reactions, because the overall kinetics there may depend in a complex way on the coverages of both reactants as well as on their surface mobility. Many olefin hydrogenation and H–D exchange reactions have manifested these problems [469,470]. Rough estimates for the kinetic parameters of alkene and alkyl hydrogenation steps can still be obtained with TPD experiments on surfaces saturated with hydrogen; low values, below 10 kcal/mol, have often been seen on transition metals [149,329,466].

Better kinetic data can be obtained by isothermal experiments. Sadly, though, isothermal thermal desorption experiments have been seldom performed. Alternatively, isothermal kinetic data on surface reaction steps can be acquired by using any of the surface-sensitive techniques available nowadays. All that is required is for one of the species involved, a reactant or a product, to display a unique and prominent spectral feature, and for the technique to have enough sensitivity to be able to detect small changes in concentration for that surface species. The spectrometer may then be tuned to the spectral feature of interest, and the signal may be followed as a function of time as the sample is heated to the desired temperature. This idea has been used for a reasonable number of systems, by using reflection–absorption infrared spectroscopy (RAIRS) [470–472], HREELS [297,473], SIMS [474,475], laser-induced desorption [444,470,476,477], X-ray photoelectron spectroscopy (XPS) [478,479], work function [480,481], and second-harmonic generation [482], among others. Fig. 12 provides an example of how these experiments may be carried out, in this case to follow the conversion of ethylene to ethynylidyne on Pt(1 1 1) by NEXAFS [465,483]. Reaction kinetics characterized by isothermal spectroscopic methods include several hydrocarbon conversions as well as decomposition of simple molecules such as NO and alkyl halides. Nevertheless, kinetic studies lag, in general, far behind the characterization of surface species; much more work is needed in this area.

High-quality kinetic data can be obtained in some instances by using molecular beam techniques. The King and Wells approach developed for the measurement of sticking coefficients (Section 3.1) [428,429] can be extended to the evaluation of surface kinetics by following the temporal evolution of both reactants and products. Both supersonic and effusive beams have been used for this endeavor [377,393,406,484], and experiments have been carried out under transient [432,485] and steady-state [486,487] conditions. The main limitation of this technique is that it only works well for high-probability reactions, for which the products can be detected by mass spectrometry. This is the reason why most molecular beam reactivity

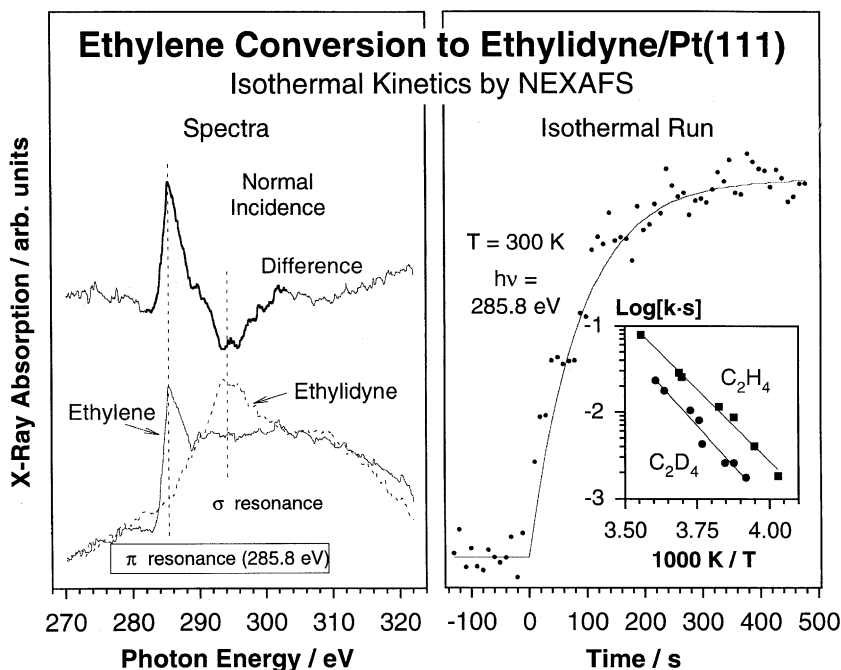


Fig. 12. Example of the use of surface spectroscopy to follow kinetics of surface reactions. The data correspond to NEXAFS measurements for the conversion of ethylene to ethylidyne on Pt(111) [465,483]. The left panel shows the normal-incidence NEXAFS spectra for adsorbed ethylene and ethylidyne species as well as the difference trace indicating the changes that occur upon thermal conversion of the former into the latter. The right figure shows a typical isothermal run (for $T = 300$ K) obtained by following the signal of the π resonance of ethylene at 285.8 eV photon energy as a function of time. The reaction displays first-order kinetics, so semilogarithmic NEXAFS signal versus time graphs were used to estimate rate constants for various reaction conditions. The inset provides Arrhenius plots for the reaction rate constants for the conversion of both C_2H_4 and C_2D_4 at different temperatures.

studies have to date been carried out on hydrogen and CO oxidation and on NO reduction. Nevertheless, kinetic molecular beam studies on ammonia oxidation [488] and on ethylene hydrogenation [409] have been reported as well. The problem of detectability may be surmountable, but requires significant experiment designing not available to date.

Thanks to the good quality of the kinetic data obtained with molecular beams, some kinetic details not previously noted have now been identified. Specifically, it has become clear that the kinetics of surface steps cannot in general be described by the simple Wigner–Polanyi-type rate laws commonly used in gas and liquid phases. Several reasons can be cited for this. First, there is always the problem of surface mobility, especially in the case of bimolecular steps. For instance, H–D exchange in adsorbed hydrocarbons can sometimes occur rapidly, but only with hydrogen and deuterium atoms adsorbed within a certain restricted area around the hydrocarbon moiety [470]. In addition, reaction energetics change with surface coverages in the

same way and for the same reasons as adsorption energies do, because of adsorbate–adsorbate interactions [377]. Then, there is the added complication of surface island formation. For instance, the reduction of NO on Rh(1 1 1) at low temperatures was found to require the build-up of a minimum coverage of nitrogen atoms on the surface [489]. Results from isotope-labeling beam-switching experiments strongly suggest that those N atoms coalesce into surface islands [489–491], and that only the atoms at the periphery of such islands are available to react with fresh NO molecules to produce N₂ via a N–NO-type intermediate [490,492]. Finally, the kinetics of some surface steps may depend not only on the coverages of the reactants, but also on the history of the chemical process. Fig. 13 illustrates how the rate for carbon monoxide oxidation on Pt(1 1 1) can vary widely depending on the method used to prepare the surface [493]. It is argued that oxygen atoms in islands are more reactive because of a

Dependence of Surface Reaction Rates on the Spatial Distribution of Adsorbates

CO Oxidation on Oxygen-Covered Pt(111)

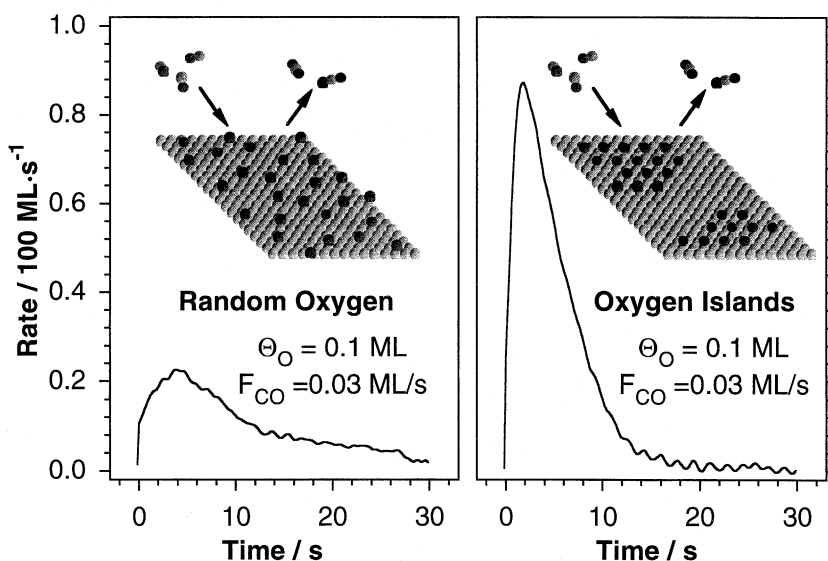


Fig. 13. Oxidation kinetics for carbon monoxide on oxygen-covered platinum single-crystal surfaces pointing to the importance that the spatial distribution of the adsorbates has in determining reaction rates [493]. Two different sample preparation methods were used, to obtain a random distribution of O atoms on the surface in one case (left), and a clustered arrangement in ordered surface islands in the other (right). Large differences in rates were observed between the two cases in spite of the fact that both kinetic runs started with the same average concentrations of oxygen and CO on the surface. This example illustrates the role that neighboring adsorbates play in modifying both the energetics of the reacting species and the rates of reaction.

lowering in the adsorption energy of CO on the oxygen-covered patches of the surface.

4. Surface reaction dynamics

In addition to kinetic studies on surface reactions, the development of new spectroscopies, non-linear optical spectroscopies and scanning microscopies in particular, has allowed for the investigation of some of the fundamental aspects of the dynamics of surface processes [494]. Molecular beam work, together with more classical chemical methods and some ingenuity, has also contributed to the advance of this area. Theoretical calculations have helped in the development of this microscopic picture of surface reactions as well [495]. Below, the key knowledge derived from these studies is summarized.

4.1. Adsorption

To a first approximation, the adsorption process can be described as the approach of the adsorbate down a one-dimensional Lennard-Jones-type potential [455,496]. In this picture, the traveling direction is set as the coordinate perpendicular to the surface, and the zero-point energy at the point where the adsorbate is infinitely far from the surface. In the case of simple molecular adsorption, the adsorption energy is given by the depth of the potential well. Additional features can be added to introduce intrinsic physisorbed states and to explain dissociative adsorption. Thanks to the development of atomically resolved scanning microscopies such as STM and AFM, it has been possible to measure these potentials directly [497,498].

Adsorption is in most cases non-activated, which means that the molecule finds no energy barriers as it travels towards the surface. Therefore, gas-phase molecules have to dissipate their kinetic energy in order to become trapped in the adsorption potential well. Much experimental and theoretical work has been dedicated to the understanding of the energy transfer from the incoming molecule to the solid substrate [499]. Typically, the excess kinetic energy of the impinging particle is transferred either to the vibrational modes (phonons) of the solid lattice [25,500], the preferred path to physisorption, or via electron excitation (electron-hole pair formation) [501–504], often the case in chemisorption.

In the simple one-dimensional picture given above, only the momentum perpendicular to the surface needs to be transferred to other excitation modes, so the trapping probability scales with the normal component of the kinetic energy of the impinging particles. This “normal energy scaling” holds true for a good number of adsorption systems [500,505]. However, many other cases deviate significantly from such simple prediction [506]. In fact, there is some degree of corrugation in the potential within the plane of the surface, and, as a consequence, a true representation of the gas–solid interaction requires the use of multi-dimensional potentials. In particular, it is quite possible for some kinetic energy to be transferred from the normal to the parallel component of the motion of the adsorbate with respect to the

surface as the adsorption takes place. This energy transfer does not in itself result in real trapping, only in an increased mobility across the surface, but that leads to longer times near the surface, thus enhancing the probability for energy exchange [500]. The same reasoning applies to the transfer of kinetic energy to rotational or vibrational states of the molecule [507–509]. Some interesting recent papers report direct evidence for the strong dependence of adsorption on the relative orientation of the molecule when colliding with the surface, at least at low kinetic energies, suggesting the relevance of steric factors in chemisorption probabilities [510,511].

Adsorption probabilities usually display a weak dependence on temperature. In the case of non-activated adsorption, sticking coefficients tend to decrease slightly with increasing gas and/or surface temperatures, presumably because the higher the temperature the more kinetic energy the gas molecules have to dissipate [29,500]. The decrease in sticking with increasing gas energy is illustrated by the data for NO on Ru(0001) shown in the left panel of Fig. 14 [403]. On the other hand, since dissociative adsorption usually goes through a molecular physisorbed state, it can be activated [512]. The right panel of Fig. 14 displays the case of oxygen on W(110), for which activated adsorption results in a stepwise increase in the sticking coefficient with kinetic energy [512]. A number of theoretical models, including the “hard cube” model [513–515] and its derivations [516,517], quantum-mechanical theories [518],

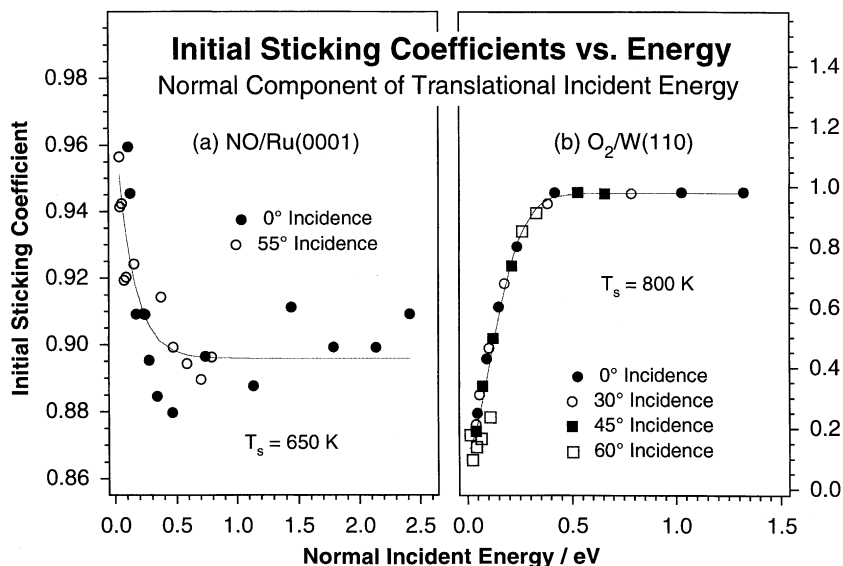


Fig. 14. Dependence of initial sticking coefficients on kinetic energy of the incident gas-phase molecules. Data are shown for two systems, for the adsorption of nitrogen monoxide on Ru(0001) (left, [932]), and for the uptake of oxygen on W(110) (right, [512]). In both cases the sticking coefficients were found to scale with the normal component of the incident energy, $E_{\perp} = E_i \cos^2 \theta$. However, while the sticking coefficient of NO decreases with increasing energy, the opposite is true for O_2 . The latter behavior is typical of activated adsorption processes.

and trajectory calculations [519–522], have been reasonably successful in accounting for all these observations [500].

4.2. Desorption

Since desorption represents the reverse of adsorption, the same potential energy surface should be able to describe both processes [523]. Moreover, if equilibrium is assumed at all stages of the desorption, the principles of microscopic reversibility and detailed balance allow for the direct inference of desorption dynamics from the knowledge acquired in adsorption studies (and vice versa) [524,525]. Molecular beam work has been combined with studies on the angular and energetic distribution of desorbing species to put together a coherent picture for the potential governing adsorption and desorption processes.

If the surface is considered to be structureless and the adsorbate in equilibrium with the solid, the angular distribution of the desorbing species is expected to follow a simple cosine dependence, and their energy distribution to be Maxwellian [526]. Early examples provided some evidence for this [527,528]. On the other hand, it has been known for some time that all surfaces present some structure. Even basal planes of single crystals display the potential corrugations responsible for the existence of specific adsorption sites. However, it is quite possible for those corrugations to be too small ($\sim 20\%$ of the adsorption barrier in close-packed planes) to exert a detectable change in desorption distribution patterns; to the best of our knowledge, the effect of surface potential corrugations on desorption has not been identified experimentally yet. For instance, no structure sensitivity could be observed for hydrogen desorbing from different faces of nickel [529].

In spite of the success of the previous arguments, early studies on hydrogen desorption from metals by Van Willigen [530] in 1968, as well as many other reports, have identified deviations from cosine desorption profiles [525,531–533]. The same can be said for non-Maxwellian energy distributions [526,531]. Fig. 15 shows an example where both Maxwellian and non-equilibrium desorption are seen, that of deuterium desorbing from sulfur-covered Pd(100) [534]. These deviations have been explained in terms of adsorption energy barriers. In connection with this, it is interesting to note that highly peaked desorption profiles have so far been reported for products of bimolecular reactions, either for the recombinative desorption of hydrogen, oxygen or nitrogen [525,526,530,535], or for the oxidation of carbon monoxide [533,536–540]. Some recent investigations have also identified vibrationally hot desorbing molecules [541–543]. Unfortunately, the number of systems for which the details of desorption dynamics have been investigated is still relatively small, so it is too early to propose sweeping conclusions in this field.

4.3. Unimolecular steps

Probing the dynamics of surface reaction steps is much more difficult than looking into the dynamics of adsorption–desorption processes, and little work has been done

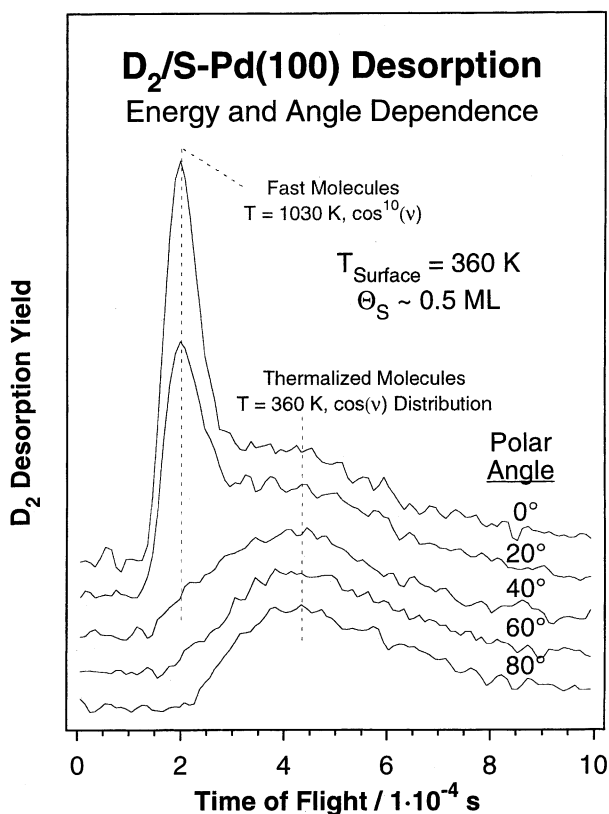


Fig. 15. Time-of-flight measurements for the desorption of deuterium from a Pd(100) surface poisoned with a small amount of sulfur atoms [534]. The kinetic energy distribution of the outgoing molecules was measured for a number of desorbing angles. Two desorption distributions are seen in this system, one peaking around 0.45 ms corresponding to thermalized molecules with an average kinetic energy of 360 K (the same as the surface) and a cosine angular distribution, and a second centered about 0.2 ms associated with fast molecules with an angular distribution highly peaked about the surface normal.

in this area to date. Only in a few instances have there been reports on the details of surface elementary steps, mostly on the nature of the transition state. In the case of unimolecular steps, a combination of old-fashioned chemical ideas have been employed to look into the dehydrogenation of hydrocarbons, including isotope labeling and group substitutions (Fig. 16). Specifically, a number of regiospecific labeling experiments were used to establish that the dehydrogenation of surface alkyl groups occurs selectively at the beta position [310,328,330,333,544]. The hydride nature of the leaving group was initially inferred by analogy with organometallic systems [79,231,327], and later corroborated via the use of inductive effects by selective fluorine substitutions [545,546]. Also by analogy with reactivity studies on inorganic discrete molecules, the four-center planar geometry of the transition state was probed via structural analysis with strained cyclic molecules [146,547]. Theoretical cal-

β -Hydride Elimination Mechanism

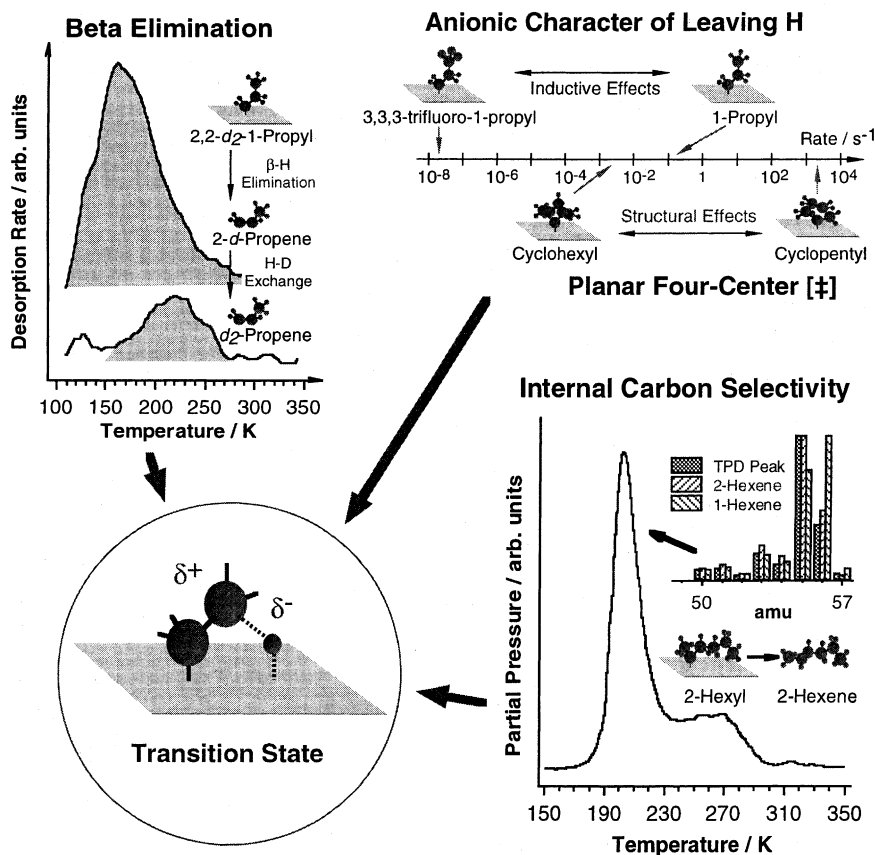


Fig. 16. Representative data from substitution studies used to determine the nature of the transient state in β -hydride elimination from adsorbed alkyl groups. Top, left: the preferential desorption of mono-deuterated propene from thermal decomposition of 1-propyl-2,2- d_2 groups on Ni(100) indicates that hydrogen removal occurs selectively from the β -carbon [333]. Top, right: the large change in dehydrogenation rate on Cu(111) induced by substitution of the γ -hydrogens in 1-propyl groups with fluorine points to the anionic nature of the leaving β -hydrogen [545]. Also, the changes resulting from the constraints imposed by the structure of cyclic (1-cyclopentyl versus 1-cyclohexyl) alkyls on Cu(100) suggest a planar four-center transition state [547]. Bottom, right: Hydrogen atoms are extracted from inner (more substituted) carbons, hence the selectivity for 2-hexene formation from 2-hexyl adsorbates on Cu(100) [329]. The four-center planar transition state proposed for this β -hydride elimination step is shown schematically in the lower left corner.

culations support the ideas developed from these experiments [548,549]. Unfortunately, this is a unique example in surface science; the systematic substitution experiments routinely used in other areas of chemistry have yet to be fully exploited in surface studies.

The best tool available nowadays for the evaluation of reaction pathways on surfaces is computer simulations. A number of groups have addressed the mechanistic details of several surface steps this way, including the dissociation of diatomic molecules [550–552], the activation of methane [553–555], and others [556–561]. Great progress has been made in recent years in terms of the quality of those simulations, but much more is needed before subtle questions associated with selectivity or coverage-dependent rates can be properly addressed [562].

There have also been some attempts to characterize energy transfer mechanisms at surfaces directly via optical pump–probe time-resolved experiments [563,564]. So far, most of the information from those studies refers to vibrational or electronic excitation and relaxation of simple adsorbates [565–568], but a few studies on reactions such as carbon monoxide oxidation are starting to appear in the literature [569]. Even photo- and electro-decomposition steps on single molecules have now been observed by STM [570]. However, the application of these techniques to the study of surface reactions is still in its infancy.

4.4. *Bimolecular steps*

When considering bimolecular surface steps, one of the key issues in terms of reaction dynamics is the way the two reactants come in contact with each other. Traditionally, two extremes have been identified for this [1]. At the one end, surface reactions may take place among atoms or molecules adsorbed in adjacent sites. This mechanism, termed Langmuir–Hinshelwood (LH), requires the adsorption of both reactants and the fast diffusion of at least one of the reactants on the surface [571]. At the other extreme, chemical reactions may occur as the result of collision of a gas molecule with a surface adsorbate, the Eley–Rideal (ER) mechanism [17]. The catalysis community had long favored the LH route, but direct evidence for this had to wait for the development of molecular beam methods. It was only in 1978 that Engel and Ertl [572] showed that there was a time delay between the impinging of CO molecules on an oxygen-covered Pd(111) surface and the release of the CO₂ product, proving unequivocally that such a reaction proceeded via the reaction of two adsorbed species. This conclusion has since been generalized to many other surface reactions.

The gathering of evidence for the ER mechanism has been much more difficult, but has advanced considerably in recent years, again thanks to molecular beam techniques. The most studied family of systems in this context has been the abstraction of surface adsorbates by incoming hydrogen atoms or molecules [573–577]. The non-Boltzmann distribution of H₂ molecules desorbing in a highly peaked distribution in those experiments has been taken as evidence of a direct reaction between gas-phase and adsorbed species. A number of theoretical calculations have supported this interpretation [578–580].

The applicability of the ER mechanism to other reactions has also been addressed in recent reports. For instance, the kinetics of the reaction of gas-phase D atoms with methyl moieties adsorbed on Cu(111) at 100 K leads to the formation of CH₃D molecules at temperatures as low as 100 K, too low for an LH step (which requires

about 300 K) [581]. The displacement of halide atoms in halohydrocarbons adsorbed on carbon-covered Pt(1 1 1) by incoming gas-phase D atoms has also been interpreted in terms of ER dynamics, given that hydrogen does not adsorb on such a surface [582]. Perhaps the most convincing and interesting example of ER chemistry for catalysis is that of the hydrogenation of olefins by gas-phase atoms. In a series of elegant experiments, Xi and Bent [323] have shown that olefin hydrogenation on copper can only take place when H atoms impinge onto the surface, not when alkenes are adsorbed on a surface precovered with hydrogen atoms. The stereochemistry of that ER process was also studied with reference to the addition of hydrogen to cyclohexene on Cu(100) in order to take advantage of the rotational restriction about the C–C bond in the alkyl product [583]. It was shown that H addition to the C=C double bond (which is oriented parallel to the surface plane) occurs from the top face (vacuum side). Addition of gas-phase methyl groups to adsorbed phenyl groups has also been reported [584].

The LH and ER mechanisms can be seen as extremes of a range of reaction dynamics that depend on the degree of energy accommodation of at least one of the reactants on the surface before reaction. It is possible for reactants from the gas phase to not dissipate their entire excess kinetic energy before colliding with a second adsorbate, or for adsorbed molecules to dissociate and eject energetic particles towards a second adsorbate. These “hot” adsorption precursors and adatoms open

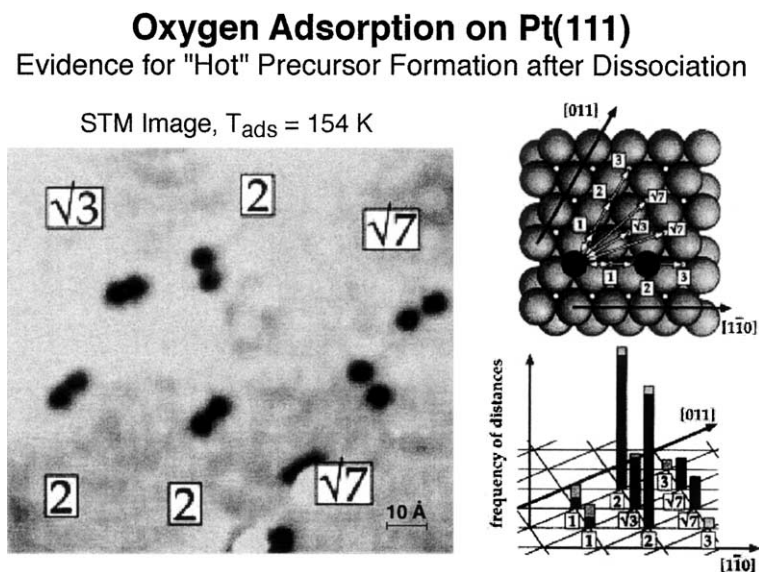


Fig. 17. Dissociative adsorption is often followed by lateral motion of the resulting fragments until the excess energy is dissipated. The STM image shown in this figure displays a typical distribution of oxygen atoms obtained after dissociative adsorption of O_2 molecules on Pt(111) at 154 K [589]. The statistical analysis shown in the lower right corner provides evidence for a non-thermal diffusion process for the O atoms right after dissociation. It was concluded that some transient ballistic motion takes place in this case. The short distances traveled by the atoms agrees with recent molecular dynamics studies.

new avenues for reactions between two species on surfaces [505,585,586]. Evidence for both molecular “skidding” along the surface during chemisorption [587,588] and ballistic ejection of hot atoms upon surface dissociation of adsorbed molecules [589,590] has been obtained by STM. Fig. 17 shows some of the STM data obtained for the dissociative adsorption of O_2 on Pt(1 1 1) supporting the latter phenomena [589]. The participation of hot atoms in surface reactions is just beginning to be probed [499,591].

5. Surface reaction mechanisms

So far, the discussion in this review has centered around the isolation and characterization of surface intermediates and about the identification of surface elementary steps. In fact, catalytic processes are often quite complex, involving many such elementary reactions. The next task in the surface-science studies of catalysis is to break down overall catalytic processes into their elementary components in order to come up with a complete mechanistic description. In this section, both some of the advances made in this direction and a few of the difficulties associated with this work will be discussed.

5.1. *Relevant intermediates*

It has been long recognized that the presence of specific adsorbates on the surface during catalysis does not ensure their direct role in the catalytic process. In fact, it has often been said that if a surface species can be seen, it is not important for catalysis. Although this latter statement represents an extreme and not always justified view, it does bring about a healthy level of skepticism to the study of the surface chemistry of catalysis. One of the first tasks in determining reaction mechanisms is to identify relevant reaction intermediates.

A good example of how surface science can help in this endeavor can be seen in the work on the epoxidation of ethylene over silver surfaces. Extensive studies on this system led to the identification of three different types of oxygen: molecular, atomic, and sub-surface [592–595]. From these, surface-science experiments were able to point to a direct connection between atomic surface oxygen and ethylene oxide production [596,597]. Carbon dioxide production was connected to the same atomic oxygen species, but selectivity towards partial oxidation (ethylene oxide production) was deemed to be influenced by sub-surface oxygen [593,597]. The changes in selectivity due to the latter species may be related to electronic modifications of the surface, in the same way as when induced by the alkali metals and chlorine often added to this system [598,599]. Molecular oxygen appears to play no direct role in the reaction.

Another well-developed example of the formation of surface species not directly connected to catalytic reaction mechanisms is that of the deposition of carbonaceous deposits during hydrocarbon hydrogenation and reforming processes [150,249,290]. In the case of olefin hydrogenation, it has been established that the surface of the

catalyst is almost fully covered with strongly adsorbed species, typically alkylidyne, during those reactions [240,248,600]. It has been shown that such deposits do not participate directly as intermediates on the way to hydrogenation products [149,408,601], but otherwise their exact role in the hydrogenation process has been highly contested. Most likely, strongly adsorbed hydrocarbon fragments passivate the surface, allowing for more weakly adsorbed intermediates to hydrogenate [409]. The mechanistic details of this system are complicated further by the significant changes observed when going from vacuum to atmospheric pressure conditions. This will be addressed in greater detail in Section 7.5.

5.2. Sequential steps

In many cases, the conversion of surface species occurs almost immediately after activation of the reactant. In other words, the chemistry of many adsorbates is often limited by the initial step. This is particularly common in complex hydrocarbon conversions [380,602]. For instance, alcohols usually form alkoxide intermediates on metal surfaces at low temperatures, but then decompose to H_2 and CO [164,171]. In those situations, the intermediates involved in the middle steps are hard to isolate; the products of multiple sequential steps are detected instead. In order to elucidate the mechanism of such reactions, a bit of detective work needs to be carried out, and the chemistry of potential intermediates needs to be investigated by alternative routes.

The research on the mechanism for the conversion of olefins to alkylidynes on transition-metal surfaces, for the conversion of ethylene to ethylidyne on Pt(1 1 1) in particular, illustrates well the difficulties in identifying sequential steps. Given that the conversion of adsorbed ethylene ($Pt-CH_2-CH_2-Pt$) to ethylidyne ($Pt_3\equiv C-CH_3$) requires the abstraction of one hydrogen atom and the migration of another, it is reasonable to assume that the mechanism for such a conversion consists of at least two steps, and, as a consequence, involves the formation of one or more intermediates. Initial proposals favored an ethyl ($Pt-CH_2-CH_3$) intermediate [603], but TPD and infrared spectroscopy data from ethyl iodide on Pt(1 1 1) indicated that ethyl groups convert back to ethylene via β -H elimination at temperatures much lower than those required for the formation of ethylidyne [330,544,604]. The formation of a vinyl ($Pt-CH=CH_2$) intermediate was first suggested on the basis of the unexpectedly large H_2 desorption seen from trideuteroethylene ($CD_2=CDH$) [605]. SIMS data from vinyl iodide on Pt(1 1 1) later supported the idea of a direct conversion of vinyl to ethylidyne on Pt(1 1 1) around 120 K [234], but infrared spectroscopy experiments did not confirm that low-temperature step [235]. At this point, ethylidene ($Pt=CH-CH_3$) seems to be the most likely intermediate for the formation of ethylidyne from adsorbed ethylene, although the mechanistic details of this reaction appear to change with surface coverage (see Section 7.4 and Fig. 18) [322,337,606].

5.3. Parallel steps: competition and selectivity

Besides sequential steps, the surface conversion of surface species may also involve parallel reactions. Understanding parallel reactions is particularly important in

Competition among surface steps is possible in most systems [492], but is particularly prevalent in the surface conversion of organic molecules [79,150,170,171,178,334,602]. For instance, the selectivity between partial and total hydrocarbon

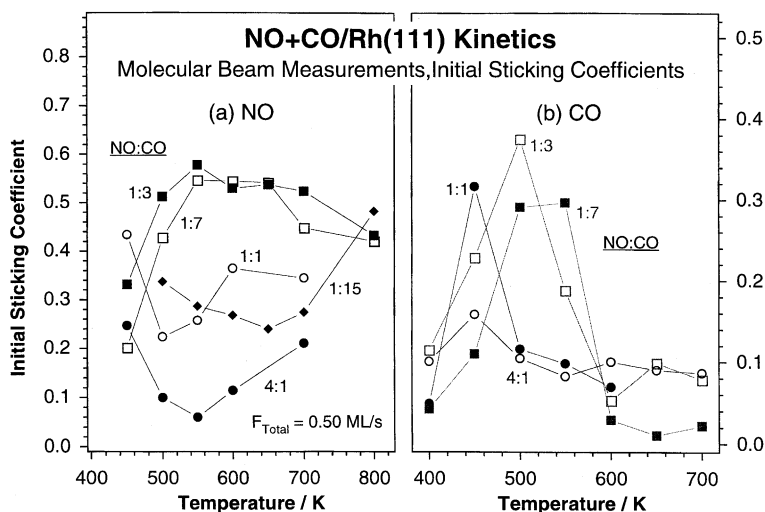


Fig. 19. Initial sticking coefficients for the adsorption of NO (s_{NO}^0 , left) and CO (s_{CO}^0 , right) from NO:CO beams on a Rh(111) as a function of surface temperature and beam composition [432,490]. The total flux was kept constant in all these experiments at $F_{\text{Total}} = 0.50 \text{ ML/s}$. In general, s_{NO}^0 goes through a maximum at the conditions required for optimum surface stoichiometric NO and CO coverages, while s_{CO}^0 often starts to decrease at lower temperatures than s_{NO}^0 . More generally, these apparent sticking coefficients change significantly with gas-phase composition, an observation that points to the competitive nature of the adsorption.

oxidation often depends on surface coverages and temperature [170,379,380]. In the case of olefin conversion on transition metals, molecular desorption, hydrogenation, H–D exchange, and decomposition reactions all take place within the same narrow range of temperatures, so small changes in relative rates result in significant changes in selectivity [150,466,470]. This may very well be the reason for the unique performance of platinum in hydrocarbon reforming processes [342,607].

One interesting subset of competing processes is that related to the simultaneous occurrence of molecular desorption and surface conversion in the same temperature range. The particularly common nature of such competition brings into question the exact dynamics involved. An extreme of this is seen in the simultaneous desorption of hydrogen and CO in a sharp desorption feature when coadsorbed on Ni(100) surfaces [608,609]. Several explanations have been offered to account for that behavior, including surface reconstruction, stabilization of new adsorbed states, and island formation [610,611], but none has been proven conclusively. Another amusing observation is that of “explosive” desorption, as seen, for instance, during the decomposition of formic acid on Ni(110) [612], or in connection with the desorption of nitrogen from Cu(111) [613]. Autocatalysis has been mentioned as the reason for such kinetics. Oscillatory reactions also involve complex kinetics requiring autocatalysis [614]. What is clear is that cooperative effects play a role in all those cases, most likely involving energy transfer in non-equilibrium dynamics of the sort discussed in Section 4.4.

6. Extension to real systems

The studies summarized above have for the most part been carried out with clean single-crystal surfaces and under well-controlled vacuum conditions. The question arises on the relevance of those studies to catalysis. On the one hand, the local adsorbate-surface chemistry is expected to be the same regardless of the conditions of the experiments. On the other, higher pressures allow for the steady-state formation of weakly adsorbed intermediates in significant concentrations. In addition, the complexity in surface structure introduced by the nature of the supported catalysts provides many new potential reaction sites. In this section, work done to extend surface-science studies to realistic conditions is reviewed.

6.1. Pressure gap

The high (atmospheric) pressures used in catalytic processes open new avenues for gas reactivity. This is so mainly because higher pressures means higher impinging frequencies for the gas molecules, and that allows for the build-up of larger surface concentrations of weakly adsorbed species (the gas-adsorbate equilibrium shifts towards the adsorbate side because of the increase in the forward reaction rate). The reactivity of such weakly bonded intermediates is difficult to probe under vacuum. This so-called pressure gap has been addressed by a number of research groups with mixed success.

From the experimental point of view, the first great advance in bridging the pressure gap was the development of what has become known as the high-pressure cell, a device that allows for the direct transfer of small solid samples directly between vacuum and atmospheric catalytic conditions [615]. That permits the post-mortem analysis of catalysts with modern surface-sensitive techniques right after the catalytic processes, and with that the correlation of surface properties with catalytic activity [616]. Studies with this equipment have been carried out on nitrogen oxide reduction [617], carbon monoxide hydrogenation and Fischer-Tropsch reactions [618–622], carbon monoxide oxidation [623], ammonia synthesis [624], alkane activation [625,626], and hydrocarbon hydrogenation [248,627], reforming [628–630] and hydrodesulfurization [631], among others. More recently, in-situ characterization techniques have been incorporated to this type of studies, optical spectroscopies (infrared spectroscopy [632–635], second-harmonic and sum-frequency generation [177,600,636]) and scanning microscopy [452] in particular. Fig. 20 displays infrared spectra obtained during the catalytic reduction of NO by CO on Rh(111) inside one of those cells [637]. This experimental approach promises to open the door for the direct identification of reaction intermediates during catalysis.

The efficiency of different solids in promoting specific catalytic processes is often related to the adsorption energies of the reactants and products. If the reactants interact too weakly with the substrate, they desorb before reacting. On the other hand, if the species involved adsorb too strongly, they may not desorb but poison the surface instead. There is an optimum middle range for adsorption energies for the catalytic cycle. This is typically represented by volcano-shaped plots of reactivity

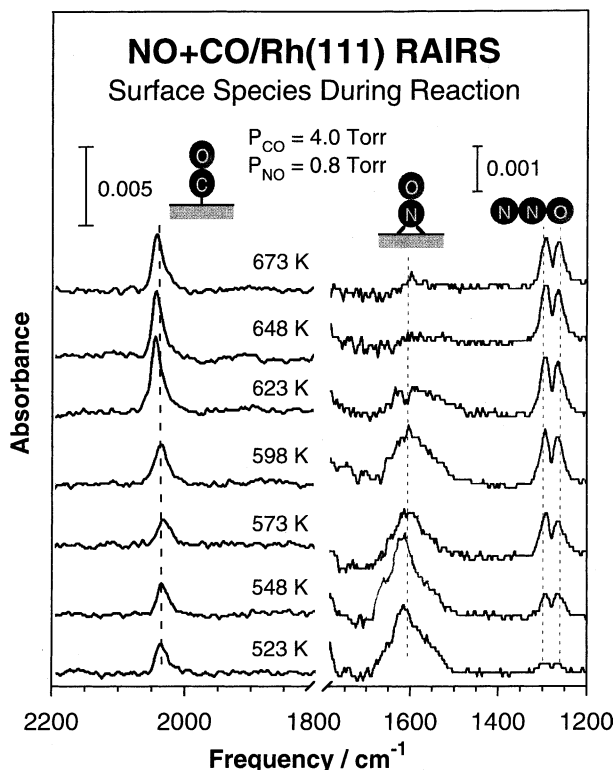


Fig. 20. RAIRS spectra taken in situ during the catalytic conversion of CO + NO on Rh(111) at close to atmospheric pressures [637]. Spectra were taken for a 4.0 Torr CO + 0.8 Torr NO mixture as a function of surface temperature. A number of surface intermediates were identified, atop CO and bridged NO in particular (as well as gas-phase N_2O). A transition is observed in the populations of adsorbates during reaction as a function of temperature: while the surface is mostly covered with NO at low temperatures, almost exclusive CO is seen as the surface is heated.

versus heats of adsorption [1,638]. The exact energy range useful in catalysis depends on the particulars of the process, specifically the temperature and pressures required. According to the severity of the changes in reactivity observed when changing catalyst preparation procedures, catalytic reactions can be ranked between two extremes [639]. On one end, demanding reactions such as ammonia synthesis and CO, NO_x , and hydrocarbon oxidation typically require high pressures and temperatures. At the other extreme, non-demanding reactions, hydrogenation of unsaturated hydrocarbons in particular, take place under mild conditions (atmospheric pressures, room temperature). The two types of reactions may follow significantly different kinds of mechanisms.

It is generally believed that during the steady-state regime of demanding catalytic reactions the surface is covered with small concentrations of strongly bonded intermediates similar to those characterized by vacuum surface analytical techniques.

Because of this, the knowledge acquired by surface-science studies is likely to transfer directly to catalysis. In the case of methane activation, for example, catalytic kinetic runs on single crystals have been successfully used to reproduce data obtained using real supported catalysts [620]. Much has been learned about the initial activation of methane [640–644] and about the chemistry of the resulting methyl surface groups [146,233,329,332,335,336,645] by studying appropriate controlled systems under vacuum. That knowledge is being used to design viable commercial processes for the conversion of natural gas to more useful chemicals.

Non-demanding catalytic processes, on the other hand, present a much bigger challenge for the surface-science community. It has become clear that the surface of the catalysts used in those processes becomes covered with large amounts of strongly held surface species during the steady-state reactions, but the role of those moieties has not yet been elucidated. As already discussed in Section 5.1 with reference to carbonaceous surface residues, what has been shown so far is that such species are not direct participants in the mechanism of the relevant reactions, but play an indirect role instead. In the case of hydrocarbon conversions, for instance, the carbonaceous deposits that grow on the surface are believed to store hydrogen, and to perhaps passivate the metal to avoid deep dehydrogenation and decomposition of the reactants [150,249,290] so more weakly adsorbed intermediates can participate in the catalytic process [229,409,600,633,646]. Unraveling the role of strongly and weakly bonded surface adsorbates in non-demanding reactions will require a great deal of creativity.

6.2. *Materials gap*

Another source of divergence between the chemistry of simple model systems and real catalysts is often referred to as the materials gap. This gap has to do with the fact that the size and shape of the particles in supported catalysts influence their chemistry in ways not easy to reproduce with single crystals, foils, or films. For one, the electronic properties of many solid particles, of metals in particular, change dramatically as their diameter becomes smaller than 10–100 Å; most supported catalysts involve particles in that size range. Moreover, catalytic particles often interact in complex ways with their supporting surfaces (typical catalysts are composed of an active phase finely dispersed on a high-surface-area solid). In fact, the performance of some catalysts depends in part on the activity of the support itself. Reforming catalysts, for instance, rely as much on the acidic functionality of the silico-alumina support as on the hydrogenation–dehydrogenation activity of the active transition metals [15]. It is also possible for adsorbates to spill over from one phase, where they are produced, to another, where the final reactions take place [647]. Finally, in extreme cases, a strong metal–support interaction (SMSI) makes the catalyst perform in ways not accountable by either phase alone [648]. None of these phenomena can be easily studied by using single crystals.

The complex structure of solid surfaces is of great relevance to catalysis, since it provides a vehicle for the existence of special sites not available in discrete molecules. In fact, it is the strong dependence of the rates of some reactions on the structure of

the catalyst that makes heterogeneous catalysis so useful. This correlation between surface structure and reactivity has been explored in the past via controlled surface-science studies on single crystals with different exposed planes. Somorjai and co-workers pioneered this work by first determining the stability of surface planes with different degrees of steps and kinks [25,649], and by then performing chemisorption experiments on those substrates [650,651]. The role of steps in catalysis became quite evident in molecular beam studies on the $\text{H}_2\text{--D}_2$ isotopic exchange over platinum single-crystal surfaces [652]. It was shown that the activity of that reaction increases dramatically when the beam is oriented towards the bottom of the surface steps (Fig. 21). More recently, RAIRS [376,377,653] and STM [654,655] work has shown the importance of steps and kinks more directly. It appears that, in general, steps and other low-coordination sites display higher reactivity than flat terraces for catalysis [656], and that it may often be the bottom of the step where activation of adsorbates takes place [657].

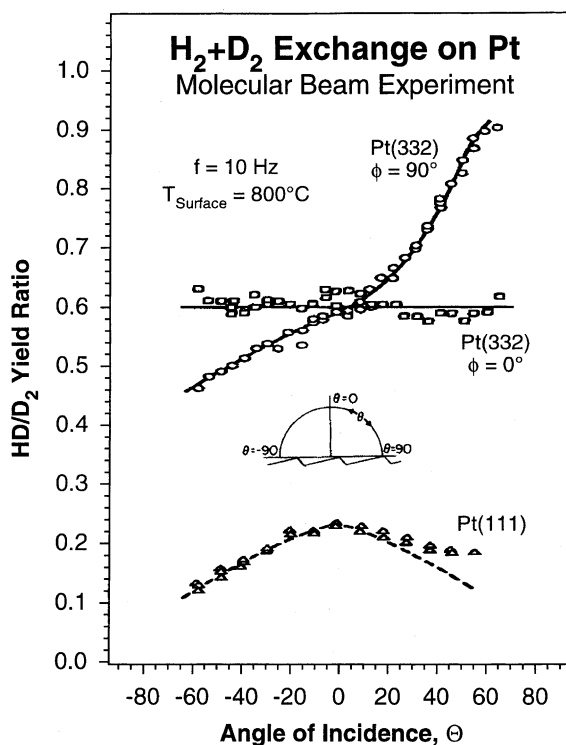


Fig. 21. Molecular beam work highlighting the key role of surface steps in catalysis. The data shown here correspond to the HD produced by isotopic exchange between H_2 and D_2 on platinum surfaces as a function of the angle of incidence of the reactants [652]. Only a weak dependence of activity on angle is seen on Pt(111), where the conversion probability is in general quite low. On the stepped Pt(332) plane, on the other hand, a significant increase in reaction rate is observed when the beam is aimed at the bottom of the surface steps.

One pristine example of the effect of surface structure on catalytic activity comes from the study of ammonia synthesis from molecular nitrogen (the Haber process). Dramatic differences in both dissociative adsorption probabilities for N_2 [126] and ammonia production rates [624,639] have been reported for iron surfaces with different structures. Two main conclusions were reached from that work: (1) the rate of ammonia production is limited by the initial dissociative adsorption of the nitrogen molecule; and (2) specific so-called C_7 sites are needed for N_2 activation. The latter conclusion is of great significance for the design of ammonia synthesis catalysts, and appears to also extend to the activation of carbon monoxide in Fischer–Tropsch processes [658].

The majority of traditional catalysts are based on supported transition-metal particles. Consequently, surface-science studies have mostly focused on those materials. Nevertheless, new catalysts rely on the unique properties of more complex materials such as alloys [659–661], oxides [194,662,663], carbides [201], nitrides [664–666], sulfides [318,667,668], and other covalent solids. Understanding the characteristics of the catalytic site is especially important in those systems. Oxides in particular have received substantial attention in recent years. Unfortunately, most studies have focused on a handful of oxides, noticeably TiO_2 [669–672], Al_2O_3 [673–675], SnO_2 [676], NiO [197,416,677], and MgO [442,674,678], although studies on a few others are starting to appear as well [679]. One problem with this research has been that the basal planes of most oxides are inert, displaying no interesting chemistry except perhaps for the conversion of some oxygenates [680]. Higher activity can be seen on defective surfaces, but the exact nature of the active sites has not yet been fully determined, and a direct correlation between the existence of specific sites on the surface and the activity of the catalyst is yet to be established [680]. Oxygen and cation vacancies and substitutions (F and V centers) [669,671], dislocations and point defects [681], reduced or oxidized surface metal atoms [682,683], and hydroxide [416,684,685], peroxides [686] and other oxygen-containing species have all been invoked to explain catalytic processes. Hydroxides in particular appear to have a unique role in improving the selectivity towards partial oxidation reactions [380,670,687]. Aggregates of F centers (oxygen vacancies) have been recently correlated with the sites required for methane oxidative coupling [688].

A combination of chemical and physical methods can be used to prepare and characterize specific defect sites in situ on well-defined substrates. For instance, low-coordination nickel sites in nickel oxide can be titrated by CO adsorption [689]. Oxygen vacancies can also be titrated via the conversion of NO to N_2O , H_2O to H_2 , or formaldehyde to ethylene [690,691]. Further reactivity studies on surfaces with high concentrations of specific surface ensembles will be able to address this structure–reactivity correlation issue directly.

The chemistry of adsorbates on alloys has also been studied in some detail, but is still far from understood. An attempt has been made to separate the effect that one metal exerts on the other into two components, the so-called electronic and geometric effects [692–694]. In terms of geometric effects, it has been argued that the addition of a second inert metal on the surface of an active one may be

used to determine the number of surface atoms required for a given reaction. This idea is expected to work particularly well in ordered alloys, where the local ensemble of atoms is known (i.e., Sn–Pt, Si–Cu). Sadly, the chemistry observed on those surfaces is often not easy to interpret in terms of blocking of reactions requiring a large number of surface atoms [695,696]. In fact, the deposition of an inert metal layer sometimes enhances the activity of the substrate beyond that of the pure active phase: witness, for instance, the promotion of cyclohexane dehydrogenation on platinum induced by gold deposition [697]. Moreover, in most systems the element with the lowest surface tension typically segregates to the surface, making it quite difficult to control the composition of the active catalysts [698–701]. This is the reason why sometimes catalytic activity is not sensitive to changes in bulk alloy composition [702]. Lastly, the electronic properties of the alloys are hard to describe, but are most often not the result of the sum of the electronic structures of the individual components [561,659, 661,703].

Typical catalysts consist of an active phase finely dispersed on a high-surface-area support, often an oxide. The main purpose of this arrangement is to maximize the surface-to-volume ratio of the catalytic element, usually an expensive material. However, some secondary effects are often introduced this way. A number of approaches have been reported for the production of more elaborate model systems to better reproduce the complexities originating from interactions among the different components of the catalysts. In particular, metal catalysts deposited on oxide supports have been emulated by the sequential physical deposition of thin oxide films and metal particles on well-defined refractive substrates [704–706]. Fig. 22 illustrates the sequence of steps associated with this type of work, in this case for the study of palladium particles supported on a silica substrate. STM and infrared spectroscopy CO titrations were used there to establish the nature of the surface of the metal particles (~ 50 Å in diameter, with mostly (100) and (111) planes exposed), after which the catalytic activity of the model systems towards CO oxidation was checked [704]. Studies applying this methodology on more complex reactions are still in the future.

A more subtle aspect of the materials gap is the fact that the initial structure and composition of the catalysts may not be retained under the conditions of the catalytic reactions. Indeed, the fact that solid surfaces reconstruct to minimize their surface tension has been recognized for some time [286]. Adsorbates in particular are known to both induce surface structural changes and facilitate the segregation of specific components. It is therefore imperative to study catalytic surfaces *in situ* during the course of the reactions in order to characterize their active phase. This problem has barely been addressed to date. Changes in surface composition can sometimes be assessed by post-mortem analysis, but caution must be exerted when extrapolating those results to the description of the active catalyst because of the potential reversibility of the changes induced by the catalytic environment. Surface structures can also change dramatically when in the presence of high pressures of reactants, as recently documented by *in-situ* STM [707]. Again, work to answer these questions is yet to be done.

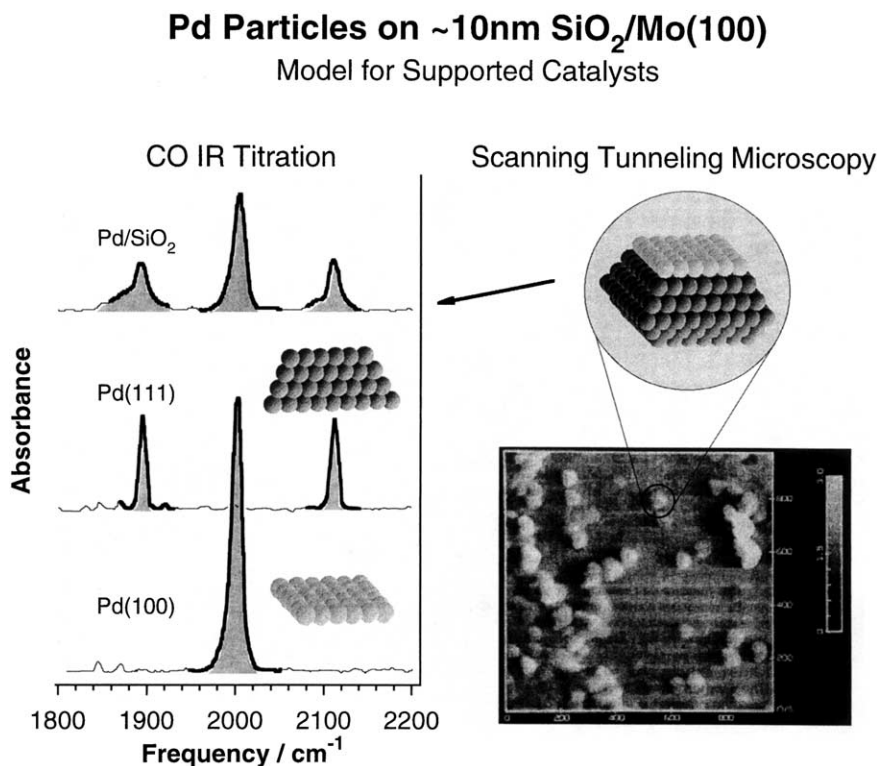


Fig. 22. Set of experimental data illustrating the steps typically followed during the development of model surfaces for the emulation of supported catalysts [704]. In this example, palladium particles were first deposited on a ~ 10 nm SiO₂ thick film (prepared by evaporation of silicon on a Mo(100) single crystal in the presence of gas-phase oxygen). Scanning tunneling microscopy was then used to determine the particle size distribution (bottom, right). It was found that this sample contained round metal particles ~ 50 Å in diameter. The surface was subsequently characterized by infrared CO titration experiments such as those illustrated in the left panel. By comparison of the IR spectra of CO adsorbed on the model catalyst to those from different palladium single crystals, the exposed surface of the metallic particles were determined to contain an approximately 1:1 mixture of (111) and (100) planes. Finally, catalytic runs were performed on this supported catalyst model system (not shown).

7. Case study: hydrocarbon conversion on transition-metal surfaces

One of the families of reactions more extensively studied by surface scientists has been the conversion of hydrocarbons on transition metals. These systems present a significant level of complexity and display quite rich chemistry, making them useful for a large number of catalytic processes of industrial interest such as oil refining, food processing, and petrochemical, speciality and pharmaceutical manufacturing, but also difficult to study. In this section, a brief overview of the progress made by the surface-science community on the understanding of hydrocarbon conversion reactions on metals is provided.

7.1. *Surface intermediates*

As soon as new surface-sensitive techniques were developed a few decades ago, they were applied to the study of hydrocarbon chemisorption [25,79]. In particular, the adsorption of olefins and other unsaturated hydrocarbons was among the first to be probed with UHV surface-sensitive techniques [149,290]. Morgan and Somorjai [74] reported LEED experiments on the adsorption of unsaturated hydrocarbons on Pt(111) and Pt(100) single-crystal surfaces as early as 1968. Extensive work has been carried out on this area ever since [148,708].

Much of the knowledge acquired from surface-science studies on olefins is exemplified by what is known about the chemisorption of ethylene on Pt(111) [149]. At low temperatures this adsorption is molecular, but involves two types of species, a low-temperature, weakly adsorbed, flat π -bonded coordination that rehybridizes above 52 K into a second flat di- σ configuration [313,709,710]. The same two types of molecularly adsorbed species have been identified for other olefins and other surfaces. The degree of double-bond character retained by the alkene upon adsorption varies smoothly with the nature of the metal involved. The extent of this rehybridization has been quantified by using a criterion based on the relative values of the frequencies of the C–C stretching and CH₂ deformation vibrational modes [237]. It has been seen olefin adsorption usually leads to significant rehybridization towards single-bond character, and that retention of the double-bond character occurs mainly in late transition metals or when species such as oxygen or carbon atoms are coadsorbed on the surface [273]. Regarding the adsorption geometry of alkenes, it most often involves coordination to a single metal atom, and results in a C–C double-bond plane oriented parallel to the surface [79,277,711]. Tilted orientations have been reported in a few cases [253,263,712].

Alkynes bind to metals in a similar manner as olefins do, except that, because of their larger electronegativity, there is more back-donation of the metal d electrons to the empty π^* antibonding orbitals of the molecule, making the bonding to the metal stronger. The molecular adsorption of acetylene has been characterized on a number of surfaces. From those studies, two types of adsorption geometries have been proposed: coordination to four atoms on W(110), Fe(111), Fe(110), Ru(0001), Ni(111), Ni(100), Pd(100), Cu(111), Cu(100), and Cu(110), and di- σ bridging coordination to either one or two adjacent metal centers with extra π interaction to the side atoms on Ru(0001), Rh(111), Ni(110), Pd(111), Pd(110) and Pt(111) surfaces [79,148,713]. Adsorption of conjugated alkenes such as butadiene is best regarded as the result of the interaction of the delocalized π system of the diene with the d orbitals of the metal, especially when the ligand is in the cis configuration. Only a few studies have dealt with the determination of the structural details of butadiene adsorbed on metal surfaces. On the one end, the adsorption of butadiene on Pt(111) leads to the initial formation of a 1,2-di- σ species at 170 K and to its subsequent conversion into a tetra- σ coordinated moiety by 300 K [151]. At the other extreme, the molecular orbitals of butadiene on Mo(100) are only minimally perturbed upon adsorption at low temperatures, but rehybridize above 200 K to convert to a moiety with an electronic configuration similar to that of gas-phase trans-2-butene [714]. No

detailed reactivity studies are available on those systems yet. Finally, benzene adsorption on metal surfaces is usually molecular at low temperatures. The aromatic ring often lies flat on the surface at low coverages [154] but sometimes tilts up near saturation [257]. The adsorption process can also induce noticeable changes in the shape of the ring (Fig. 5) [276]. Larger aromatic molecules such as toluene, *m*-xylene, and polycycles also chemisorb with the ring parallel to the surface at low temperatures [152,715]. An exception to this is tetracene on Cu(1 0 0), which adsorbs with the molecular plane in a perpendicular orientation [716].

Alkane molecular adsorption has been proposed to involve a three-center two-electron bond between a filled C–H bonding orbital and an unfilled metal d orbital [717]. The fact that many metal-based catalysts are good promoters for alkane H–D exchange and hydrogenolysis reactions is a clear indication that this alkane–metal interaction is stronger than a purely van der Waals attraction, especially in the case of heavier molecules [718]. On Ni(1 0 0) surfaces, for instance, molecular beam experiments have shown that, while the angular distribution of scattered methane displays the specular distribution typical of direct inelastic scattering, butane shows a cosine dependence indicative of complete energy exchange with the surface [412]. Temperature-programmed desorption and vibrational data suggest that the alkane chains adsorb approximately flat on the surface [719]. C–H vibrational softening has been reported in some instances [720].

It is not easy to deposit alkyls or other metastable groups on surfaces directly from the gas phase, so alternative routes have been devised to study their surface chemistry (see Fig. 9 and Section 2.4) [146,231]. As mentioned before, the most versatile and popular method for this has thus far been the activation of chemisorbed alkyl halide precursors, a method that has now been extended to the study of a large number of alkyls, vinyls, alkylidenes, metallacycles, and other hydrocarbon surface intermediates relevant to catalysis [146,231,330,721]. The success of this approach relies at least in part on the fact that the cleavage of carbon–halogen bonds, C–I bonds in particular, requires activation energies of 5 kcal/mol or less, and usually occurs at temperatures below 200 K [478,481]. The coordination of the resulting fragments to the surface appears to follow the same geometrical rules as in discrete organometallic compounds, except that coverage plays an important role in determining adsorption geometries on surfaces [79]. According to infrared and temperature-programmed desorption data, the alkyl chains initially orient themselves flat on the surface in order to maximize their interaction with the metal, but reorient to a perpendicular configuration at higher coverages, presumably because of the prevalence of van der Waals interactions between the hydrocarbon chains in that regime [251,259,722]. Unfortunately, there is no direct information on either the bonding geometry or the coordination of alkyl groups to the surface available to date. Both the low metal–carbon stretching frequency observed in vibrational studies [723,724] and some theoretical calculations [279,725] suggest that alkyls may adsorb on hollow sites, but other calculations explain the experimental results by an atop configuration instead [281]. In another example of hydrocarbon bonding geometry, vinyl groups bond in a tilted geometry, at least on Ni(1 0 0) [253]. A third case is that of alkylidynes, which coordinate on threefold hollow sites (Fig. 4) [236,322].

Some information is also available on the energetics of adsorption of hydrocarbons on metals. Olefins and other unsaturated molecules tend to bind fairly strongly on most metals, and therefore decompose rather than desorb once they are thermally activated. This makes estimating their adsorbing energies somewhat difficult. On the other hand, adsorption energies do diminish with coverage, and molecular desorption is seen at coverages close to monolayer saturation [149]. The adsorption energy of ethylene on Pt(1 1 1) has been estimated from TPD data to be about 10 kcal/mol at close to saturation [219,726]. In the case of benzene on Pd(1 1 1), two adsorption states have been reported, one tilted in a saturated layer with an adsorption energy of about 12 kcal/mol, and a second flat-lying structure at lower temperatures with an adsorption energy of approximately 30 kcal/mol [257,436]. More direct differential heats of adsorption have been recently measured for ethylene and acetylene on platinum, palladium, and nickel surfaces [727,728]. Unfortunately, those experiments have so far been carried out at room temperature, where surface decomposition obscures the meaning of the energies obtained, but this limitation is likely to be overcome soon. Finally, the metal–carbon bond energy of alkyl groups on platinum, nickel, copper, and iron have been estimated to all be similar, of the order of 30–35 kcal/mol (Fig. 8) [79,146].

7.2. *Surface elementary steps, kinetics, and dynamics on metal surfaces*

The uptake of hydrocarbons has been studied on a good number of metals. Most hydrocarbons, especially unsaturated ones, exhibit high sticking coefficients, close to one [408]. On clean surfaces the uptake is typically precursor-mediated, but the adsorption of π -bonded olefins on hydrocarbon-covered surfaces does display Langmuir behavior [409]. Desorption kinetic measurements have been closely connected with determinations of adsorption energies, and were discussed in the previous paragraph. Little is known about surface diffusion for adsorbed hydrocarbons. Olefins and other unsaturated molecules adsorb rather strongly, typically rehybridizing from π to di- σ bonding, and therefore are believed to display little diffusion. On the other hand, they tend to form ordered structures, suggesting limited mobility around the adsorption site [409].

A number of elementary steps have been identified for hydrocarbon moieties on transition-metal surfaces. Ethylene dehydrogenates to vinyl on Ni(1 0 0) around 170 K [253,476], but a much more common reaction for olefins is their complex conversion to alkylidynes [149]. From the few examples available to date, dehydrogenation of cyclic olefins appears to lead to the initial low-temperature formation of allylic surface species [162,729]. Several reports, some still contested, claim to have identified a single step for the transformation of chemisorbed acetylene into an acetylide moiety at reasonably high temperatures, above 400 K in some cases [730,731]. A couple of studies have offered some evidence for the formation of a benzyne (C_6H_4) intermediate during the decomposition of benzene on Os(000 1) [732] and Mo(1 1 0) surfaces [733], although it is not clear if this is an elementary step. The probability for alkane decomposition on metal surfaces is quite low, as manifested by their low sticking coefficients (as low as 10^{-12}), but it increases with

increasing molecular weight [734], and is likely to lead to the formation of alkyl intermediates [280].

A better understanding of the chemistry of alkyl surface species has been worked out. It has been determined that the thermal activation of alkyl groups on transition-metal surfaces is dominated by the elimination of a hydrogen atom from the beta position (the carbon adjacent to that bonded to the surface) [79,146,327,333,544]. The activation energy for that step varies somewhat with the nature of the surface, the alkyl moiety considered, and the surface structure, but it is typically of the order of 10–15 kcal/mol (Table 1) [310,342], and displays a large normal kinetic isotope effect, about a factor of ten, between normal hydrogen and deuterium atoms [150,735]. Hydride elimination from the alpha position, i.e., from the carbon directly bonded to the metal, is generally much less favorable than from the β -carbon, but it is nevertheless operative in adsorbates with no β -hydrogens such as methyl, ne-

Table 1

Estimated activation energies and reaction rates for alkyl dehydrogenation steps on nickel, platinum, and copper surfaces. Comparisons are provided for the effects of changes in transition metal, surface plane exposed, and hydrocarbon chain size and degree of branching. Rates are also contrasted for dehydrogenation steps from different positions (α , β , γ) along the hydrocarbon chain

C–H bond broken	Alkyl group	Surface	T_{\max} (TPD) (K)	E_a (kcal/mol) ^a	R (200 K) (ML/s)
β	ethyl	Ni(1 0 0)	160	9.3	200
β	<i>n</i> -pentyl	Ni(1 0 0)	190	11.1	2
β	<i>n</i> -hexyl	Ni(1 0 0)	200	11.7	0.5
β	<i>tert</i> -butyl	Ni(1 0 0)	180	10.5	10
β	<i>sec</i> -butyl	Ni(1 0 0)	210	12.3	0.1
β	ethyl	Pt(1 1 1)	180	10.5	10
β	propyl	Pt(1 1 1)	220	12.9	0.02
β	ethyl	Cu(1 1 0)	225	13.2	0.01
β	ethyl	Cu(1 1 1)	247	14.6	0.0003
β	ethyl	Cu(1 0 0)	255	15.1	0.0001
α	ethyl	Pt(1 1 1)	–	11.5 ^b	0.001 ^b
α	methyl	Pt(1 1 1)	260 ^c	15.4 ^c	0.0001 ^c
α	neopentyl	Pt(1 1 1)	≤ 250 ^c	15.0 ^c	0.0002 ^c
α	methyl	Ni(1 0 0)	230 ^c	13.5 ^c	0.01 ^c
α	neopentyl	Ni(1 0 0)	190 ^c	11.1 ^c	2 ^c
γ	neopentyl	Pt(1 1 1)	≤ 250 ^c	15.0 ^c	0.00004 ^{c,d}
γ	neopentyl	Ni(1 0 0)	–	>16 ^c	<0.0001 ^c

^a Calculated by using Redhead's equation [300] with a value of 10^{13} s^{-1} for the preexponential factor.

^b Obtained from the α - versus β -H elimination relative rates between 300 and 400 K, as determined by RAIRS data for the resulting ethylidyne from deuterium-labeled ethyl iodide.

^c Estimated from the peak of the subsequent reductive elimination of the alkyl groups with the released H. Represents an upper limit, since it assumes that the dehydrogenation is the rate-limiting step.

^d From estimated α - versus γ -H elimination relative rates using neopentane TPD traces from partially deuterated neopentyl iodides.

^e Upper limit estimated from hydrogen TPD data from partially deuterated neopentyl iodides.

opentyl, and benzyl moieties. The simplest case of an α -H elimination step is the conversion of methyl to methylene groups, first established on Pt(1 1 1) by reflection–absorption infrared spectroscopy [736]. Multiple H–D exchange was reported for methyl groups on Pt(1 1 1), suggesting an activation barrier of less than 15 kcal/mol for the dehydrogenation of those moieties [737,738]. Comparisons between α - and β -hydride elimination were performed indirectly by isotopic scrambling during high-temperature ethylidyne formation [322] and by catalytic studies with ethane on platinum [739], and indicated a rate difference of less than an order of magnitude between the two steps around 600 K. α -Hydride elimination is not only key in H–D catalytic exchange reactions, but also believed responsible for hydrogenolysis products. The latter has been corroborated for the case of the production of isobutene from neopentyl iodide on Ni(1 0 0), where the C $_{\alpha}$ –C $_{\beta}$ bond breaks after the removal of one hydrogen atom from the alpha position of neopentyl moieties [467]. The selectivity for γ - versus α -hydride elimination appears to depend on the nature of the metal surface: both steps are possible on platinum [607], while only the latter is observed on nickel [467]. This trend explains the unique ability of platinum to catalyze reforming processes, as opposed to nickel, which leads to exclusive cracking instead [342]. A set of examples of activation barriers for dehydrogenation steps from the different positions of alkyl adsorbates is provided in Table 1.

The surface-science data available on the energetics of alkyl dehydrogenation reactions illustrate some interesting trends. β -Hydride elimination from ethyl groups in particular has been reported for a number of single crystals. The following order has been found in terms of TPD peak maxima for the desorbing ethylene: 160 K for Ni(1 0 0) [740], 180 K for Pd(1 0 0) [741], 180 K for Pt(1 1 1) [310], 210 K for Rh(1 1 1) [742], 220 K for Fe(1 0 0) [743], 250 K for Cu(1 0 0) [735], 265 K for Au(1 1 1) [744], and 307 K for Au(1 0 0) [745]. As expected, the activity for this reaction generally increases (the reaction temperature goes down) when moving up and left in the periodic table. A little less is known about α -H elimination reactions, which have so far been reported mostly for methyl groups. The sequence for the desorption of the methane produced by the subsequent reductive elimination of methyl species with the α -hydrogen eliminated in that step is as follows: 168 K for Rh(1 1 1) (although this could be the result of hydrogenation with background hydrogen) [746], 170 K for Ru(0 0 1) [747], 215 K for Pd(1 0 0) [748], 230 K for Mo(1 0 0) [749], 230 K for Ni(1 0 0) [750] and Ni(1 1 1) [751], 260 K for Pt(1 1 1) [736], and 425 K for Cu(1 1 0) [329,752]. Again, these temperatures increase towards the right and bottom of the periodic table, but the changes appear to be more dramatic than in the β -H elimination case, which means that the relative rates between the two elimination pathways widen on late transition metals. Unfortunately, not much information is available on γ -elimination.

A few studies have been carried out with other potentially interesting hydrocarbon surface intermediates. Vinyl moieties usually dehydrogenate easily to acetylenes or vinylidenes [235,731], but may also couple on late transition metals such as silver to generate butadienes [753]. Aryl intermediates are more difficult to dehydrogenate, and sometimes prefer to couple to biaryl derivatives [754], or to hydrogenate to the corresponding arene [162]. Methylene has been shown to insert into metal–carbon

bonds on copper [755], but more commonly hydrogenates to methane or decomposes to surface carbon [338,736,751]. Ethylidene also dehydrogenates at quite low temperatures on Pt(1 1 1), in this case to ethynylidyne [337], but it couples to 2-butene on Ag(1 1 1) [756]. Vinylidene is known to form, at least on palladium crystals [757], but its thermal chemistry has not been well characterized. Allyls usually couple on coinage metals [340], otherwise isomerize to the corresponding alkenes [341]. Cyclohexallyl also converts to benzene [162,339,729]. Finally, metallacyclic species, which can be prepared via the activation of dihalo compounds, tend to either eliminate as cyclic compounds, or isomerize to alkenes [343–346]. One particularly interesting example of a C–C bond-forming reactions is the trimerization of acetylene on palladium [758], which involves the formation of a C_4H_4 intermediate [759].

7.3. *Surface reaction dynamics*

Studies on the dynamics of hydrocarbon adsorption have been particularly extensive for the dissociative adsorption of alkanes. Both molecular beam and adsorption–desorption techniques have indicated that the C–H bond scission in those molecules may occur either directly upon collision of the incoming gas molecule with the surface, or, alternatively, via the formation of a weakly adsorbed intermediate trapped on the surface [723,760]. The critical factor for the efficiency of alkane activation is the rate of energy transfer from the translational and internal degrees of freedom of those molecules to a particular C–H bond; the energy stored by the surface seems to be of little importance for this process [412,723,760]. An early study by Stewart and Ehrlich [761] revealed that vibrational modes are the most likely source of energy for the dissociation of methane on rhodium, and later work reported that often only the normal component of the translational energy of the alkane is important for the C–H bond-breaking step [644,762].

It has been suggested that direct alkane activation may occur via a tunneling mechanism [553], at least under the conditions encountered in supersonic beam experiments, where the molecules display a narrow distribution of high kinetic energies. The sticking probability of the alkane often increases monotonically with increasing kinetic energy, instead of displaying the threshold expected if the kinetics were dominated by an activation barrier. Also, the observed shifts in the translational energy needed to activate CH_4 versus CD_4 , or C_2H_6 versus C_2D_6 , are usually of the order of 5 kcal/mol, much larger than the differences in their zero-point energies [644]. On the other hand, the energy and angle dependence of the sticking coefficient of methane observed experimentally on some metals may be explained by a classical model that relies on the data from reductive elimination of methyl with hydrogen and the principle of microscopic reversibility [763]. In any case, the high-energy supersonic beams used in those experiments probe only a small fraction of the gas molecules in a typical catalytic mixture (those at the high-energy tail of the Boltzmann distribution). Consequently, the studies cited above suggest that the probability of any collision-induced alkane activation process is low. This has been confirmed by high-pressure experiments, which have yielded methane sticking probabilities as low as 10^{-12} [643].

Other molecular beam work has provided evidence for a precursor-mediated alkane activation mechanism. The trapping probability of ethane on Ir(110)-(1 × 2), for instance, shows only a weak dependence on the angle of incidence of the beam, suggesting that the momentum of the incoming molecules is rapidly transferred to the surface [764]. In some cases, alkane dissociation is also assisted by a reverse energy transfer from the surface to the molecule. On both platinum and rhodium, for example, the sticking probability of methane displays an Arrhenius temperature dependence in the limit of low gas kinetic energy, with an activation energy between 5 and 10 kcal/mol [765]. Lastly, physisorbed methane can be activated via collisions with other impinging molecules [373], and some heavier chemisorbed alkanes can be activated directly by heating of the substrate [766–768].

The intermediate in the trapping-mediated dissociative adsorption of alkanes most likely involves a three-center two-electron interaction similar to that in organometallic systems [79,769]. This proposal is supported by a number of observations. The activation barrier associated with the decomposition of alkanes on metal surfaces is in most cases lower than 20 kcal/mol [640,641,770], less than one-fifth of the bond energy in hydrocarbon molecules, suggesting that those C–H bonds are weakened by an electronic interaction between the alkane and the surface. In fact, soft infrared C–H stretching modes are sometimes observed in adsorbed alkanes [720]. Also, alkane activation is facilitated by electron deficiency at the metal center: early transition metals are particularly efficient in dissociating medium-size alkane chains [771], and iridium activates both methane and ethane more efficiently than platinum [772]. Rough surfaces are also in general more active than close-packed ones [772]. Finally, coadsorbed additives such as alkali metals or chalcogens can promote alkane decomposition on nominally inert substrates [773].

As mentioned in Section 4.3, one of the few unimolecular surface steps for which some dynamic information has been obtained is β -hydride elimination from surface alkyl groups. An elegant series of experiments using fluorine-substituted propyl groups on Cu(111) has demonstrated the anionic nature of the leaving hydrogen, in the same way as in organometallic systems [545]. The fact that the positive charge that develops on the β -carbon in the transition state is stabilized by electron-donating groups was demonstrated by the results from experiments with 2-alkyls on Cu(100), where the selective production of 2-olefins over 1-olefins was observed [329,547]. The large normal kinetic isotope effect observed in these β -hydride eliminations suggests that either tunneling or secondary effects may also play a role in the dehydrogenation step [146]. Some other significant trends have been observed for this reaction [79,146,328]. (1) The desorption temperature of alkenes from alkyl groups shifts to higher temperature with increasing chain length, perhaps because of the increase in adsorption energy of the products. (2) The yield for alkene production is higher for branched alkyls than for linear ones (relative to the alkane produced by the competing reductive elimination reaction), and the olefins desorb at lower temperatures. These effects can be explained at least in part by using steric and entropic arguments. (3) Open surfaces are normally more active than close-packed ones, a difference that may be correlated to the requirement of low coordination numbers for β -H elimination in organometallic complexes. (4) β -H elimination is easier on

earlier and lighter transition metals: it occurs below 200 K on nickel, palladium, or platinum surfaces, at around 230–250 K on copper, and at about 260–310 K on gold. (5) Most metals are efficient at promoting β -hydride elimination reactions, but a few late transition metals tend to favor the reductive elimination route instead. On silver in particular alkyl groups couple with 100% efficiency [331], perhaps because of the low affinity of silver for hydrogen.

Knowledge on the dynamics of bimolecular steps is particularly desirable for hydrocarbon hydrogenation steps. Most hydrogenations are assumed to occur by a Langmuir-Hinshelwood (LH) mechanism, via the insertion of the adsorbed hydrocarbon moiety into a metal–hydrogen bond. The main evidence for this comes from coadsorption experiments with H and D [149,150,162,249,466]. Interestingly, H–D exchange distributions often point to fast local reactions but limited H or D diffusion on the surface [470]. Reactions between adsorbed hydrocarbons and gas-phase hydrogen atoms are also possible. An example of this has been provided by Bent and coworkers [323,583] for the case of cyclohexene on Cu(1 0 0), where they show that H addition to the C=C double bond (which is oriented parallel to the surface plane) occurs from the top face (vacuum side). A similar addition of gas-phase methyl groups to adsorbed phenyl groups has been reported as well [584]. At the other extreme, Ceyer and coworkers [774–776] propose that hydrocarbon hydrogenation under catalytic conditions may involve hydrogen atoms absorbed (not adsorbed) on the metal.

7.4. *Surface reaction mechanisms*

As mentioned above, it has been possible to prepare and isolate most of the potential intermediates believed to participate in hydrocarbon conversion processes cleanly on single-crystal metal surfaces under vacuum. It has also been possible to study much of the surface chemistry of those species. There are, however, two overriding limitations in this work still outstanding which prevent the full use of the knowledge developed by surface chemists to the design of better catalysts. First, the thermal conversion of hydrocarbon moieties is often complex, involving many competing steps. This makes a detailed study of each individual elementary step, and the details determining selectivity, difficult. Second, it is still not clear how the chemistry observed on clean metal surfaces extrapolates to realistic high-pressure conditions. This section will address the first point, and the next the second.

Most hydrocarbon reactions observed during heating under vacuum involve hydrogenation or dehydrogenation steps. Sometimes it is possible to isolate elementary processes during those conversions; witness, for instance, the evidence on β -hydride elimination from alkyl fragments described above. However, more often multiple reactions occur either sequentially or in parallel, blurring the mechanism by which they take place. This is particularly true in the latter dehydrogenation steps leading to the formation of surface carbon and gas-phase hydrogen; almost nothing is known about how that happens. Fortunately, late dehydrogenation steps are usually not of great importance to practical catalysis, except perhaps for combustion and hydrogenolysis. It would nevertheless be useful to have a systematic understanding of the factors that control different dehydrogenation pathways.

One reaction that has elicited extensive research is the conversion of adsorbed alkenes to alkylidyne. This family of reactions has been exemplified by the conversion of ethylene to ethylidyne on Pt(1 1 1) surfaces (see Section 5.2). Ethyl, vinyl, and ethylidene moieties have all been proposed as intermediates for this reaction, but none have yet been identified unequivocally. Ethyl ($\text{Pt}-\text{CH}_2-\text{CH}_3$) intermediates were initially proposed by Somorjai et al. [603] for the ethylene-to-ethylidyne conversion on the basis of calculated activation energies, but later experimental results argued against this pathway. In particular, TPD and IR spectroscopy data from ethyl iodide on Pt(1 1 1) indicated that ethyl groups convert back to ethylene via β -H elimination at temperatures much lower than those required for the formation of ethylidyne [310,330,604]. The formation of a vinyl ($\text{Pt}-\text{CH}=\text{CH}_2$) intermediate during the conversion of ethylene to ethylidyne was first suggested on the basis of an enhancement in the desorption of H_2 from trideuteroethylene ($\text{CD}_2=\text{CDH}$) from that expected on pure stoichiometric grounds [605], and later supported by SIMS data from vinyl iodide on Pt(1 1 1) [234]. However, RAIRS experiments revealed a more complex reaction in which vinyl goes through the formation of ethylene before producing ethylidyne [235]. Finally, ethylidene ($\text{Pt}=\text{CH}-\text{CH}_3$) was initially proposed as an intermediate during the formation of ethylidyne on potassium-covered Pt(1 1 1) [777,778]. More recently, Cremer et al. [779] reported the appearance of a C–H vibration mode at 2957 cm^{-1} in sum-frequency generation (SFG) experiments during the conversion of ethylene to ethylidyne on clean Pt(1 1 1) which they assigned to ethylidene (or perhaps ethyl) intermediates. Ethylidene moieties prepared via the decomposition of 1,1-diiodoethane can in fact convert to ethylidyne surface species via a direct step at temperatures as low as 150 K [337].

On the basis of the results summarized above, ethylidene appears at this point to be the most promising candidate for the intermediate in the conversion of ethylene to ethylidyne [322]. The main argument against this proposal had come from the enhanced H_2 desorption in the TPD experiments with $\text{CD}_2=\text{CDH}$ cited before [605], but that result can be explained by an ethylene–ethylidene preequilibrium preceding the formation of ethylidyne. Our recent work with isotopic labeling has indeed shown that if ethylidyne formation involves the formation of ethylidene, the rate of the subsequent α -H elimination from that species to ethylidyne may slow down relative to its isomerization back to ethylene as the surface becomes more crowded [606]. This is understandable, because α -hydride elimination from ethylidene to ethylidyne requires empty surface sites to accommodate the hydrogen released, and those may be blocked at high surface coverages. Our data on the chemistry of 1,1-diiodoethane on Pt(1 1 1) surfaces highlighted the fact that the availability of empty surface sites plays a key role in the kinetics of ethylidyne formation [337]. The overall proposed scheme for the conversion of ethylene to ethylidyne (and, more generally, of alkene to alkylidyne) is depicted schematically in Fig. 18. A final note of caution: the spatial distribution of adsorbates also affects the course of this reaction. STM experiments have indicated that, in fact, the conversion of ethylene to ethylidyne only occurs at the interface between ethylene and ethylidyne surface islands [780].

Another critical aspect of hydrocarbon conversion is selectivity towards a specific reaction. It is often the case that adsorbed hydrocarbon species react via several

competing pathways in a narrow range of temperature. It appears that, in general, hydrogenation and dehydrogenation steps are all fast on most late-transition-metal clean surfaces, yet the net catalytic behavior of those systems changes dramatically depending on the nature of the catalyst and the conditions of the reaction. This is because small changes in relative rates result in significant changes in selectivity. In this context, it may be illustrative to compare the behavior of nickel versus platinum surfaces (Table 1). Notice that, while the first is quite effective in hydrogenolysis, the second is ideal for reforming (isomerization, cyclization, aromatization) processes. The data in Table 1 indicate that β -hydride elimination dominates on both surfaces, displaying rates several orders of magnitude higher than those for any of the other dehydrogenation steps. This implies that the preferred product from reactions with alkanes which yield alkyl surface intermediates with β -hydrogens is expected to be the corresponding olefin. This is indeed the case in most catalytic systems involving transition metals [781]. For instance, the catalytic dehydrogenation of alkanes, ranging from butanes to *n*-hexane, is at least an order of magnitude faster than any skeletal rearrangement reaction on Pt(1 1 1) [628,629]. Fast alkane–olefin equilibria are often reached in reforming catalysis. On the other hand, olefin production is a dead end on metals as far as other reactions is concerned. Consequently, β -hydride elimination plays only a minor role in hydrocarbon conversion on pure metal surfaces, although it is often critical in bifunctional reforming catalysis, where most of the skeletal rearrangements involve olefins and are promoted by the acidic sites of the support [15].

The second clear trend to be extracted from Table 1 is the fact that nickel surfaces are significantly more active towards dehydrogenation reactions than platinum. This difference amounts to a bit more than an order of magnitude for β -hydride elimination (at least in the case of ethyl moieties), but is more noticeable in C–H bond-scission steps at the α position. The higher dehydrogenation rates for nickel can easily explain its tendency to catalyze hydrogenolysis reactions [782], which are believed to involve surface intermediates with highly dehydrogenated α -carbons [783–785]. In addition, the rates for olefin and alkyl hydrogenation are comparable on Pt and Ni [150,781]. For instance, the direct reductive elimination of ethyl groups with coadsorbed hydrogen (or deuterium) occurs readily on both Ni(1 0 0) [786] and Pt(1 1 1) [310], with approximately the same activation energy, about 5–6 kcal/mol. As a consequence, H–D exchange reactions, which require a balance between hydrogenation and dehydrogenation steps, are usually more extensive on platinum than on nickel [787]. Indeed, while alkenes coadsorbed with deuterium on Pt(1 1 1) undergo repeated olefin–alkyl interconversion cycles at low temperatures and incur multiple hydrogen exchanges [149,466,470,726,788], only limited H–D exchange is observed on Ni(1 0 0) under similar conditions [336,469].

One of the most interesting observations from the data in Table 1 is that the relative rates for α - versus γ -hydride eliminations change significantly between platinum and nickel substrates [342]. Those changes were probed directly by studying the surface chemistry of neopentyl groups on both Ni(1 0 0) and Pt(1 1 1) single crystals. It was found that, on nickel, α -elimination takes place exclusively and at quite low temperatures (below 150 K), and leads to the formation of the corre-

sponding surface alkylidene [467,789]. On platinum, on the other hand, dehydrogenation starts at higher temperatures, around 250 K, and occurs competitively at both alpha and gamma positions [607]. These differences in initial dehydrogenation mechanisms affect the subsequent surface chemistry in a noticeable manner. The neopentylidene formed on Ni(1 0 0) is stable on the surface until approximately 350 K, at which point it undergoes a complex rearrangement involving the scission of the $C_{\alpha}-C_{\beta}$ bond and the formation of isobutene. Conversely, the surface species that result for the initial neopentyl dehydrogenation on Pt(1 1 1) – presumably 3,3-dimethyl platinacyclobutane and neopentylidene – remain on the surface until further dehydrogenation, which occurs in several steps starting above 400 K. More classical studies have shown that the catalytic H–D exchange of neopentane is in fact limited mostly to one methyl group, mainly yielding neopentane- d_1 and - d_3 on both nickel [790] and platinum films [791]. The exchange most likely takes place via an initial surface neopentyl intermediate, which forms after neopentane activation, and either reductively eliminates with surface deuterium to neopentane- d_1 or interconverts rapidly to neopentylidene until slowly hydrogenating to neopentane- d_3 .

Emulating skeletal rearrangement reactions under vacuum has proven quite elusive. A few examples do exist on carbon–carbon bond forming reactions, though, noticeably methylene insertion and coupling steps on coinage metals (see above). Also, the activation of methyl groups on platinum has been shown to yield ethynylidyne, and that requires the formation of a C–C bond [233]. Another interesting example of carbon–carbon bond formation is the trimerization of acetylene to benzene on palladium surfaces [758,792], a reaction that has been extended to the production of other heterocycles [793,794]. Finally, the cyclization of metallacyclic intermediates has been probed by using dihalo compounds. C–C coupling and cyclization has been observed on Ag(1 1 1) [331] and Ni(1 0 0) [344,345] but not on Pt(1 1 1) [343,346], which is surprising, since platinum is a much better catalyst for cyclization and aromatization than nickel. On the other hand, the formation of cyclohexene and benzene from 1,6-diiodohexane on Ni(1 0 0) appears to require prior extensive dehydrogenation of the α -carbons [345]. To the best of our knowledge, no hydrocarbon isomerizations have been identified under vacuum yet.

7.5. *Reactions under catalytic conditions*

An additional level of complication is added to the study of hydrocarbon conversion when atmospheric pressures are considered. This is so because it has been recognized that hydrocarbon catalysis does not occur on clean metal surfaces, but rather on metals covered with strongly bonded carbonaceous residues [290]. In retrospect, it could be easily conceived that such strongly held hydrocarbon layers are needed to passivate the surface, since it has long been known that clean metals dehydrogenate organic molecules readily until they become covered with some type of polymeric or carbonaceous deposits. ^{14}C isotopic labeling experiments have indicated that the residence time and composition of those carbonaceous species depend strongly on temperature, becoming more hydrogen deficient and more strongly held as the temperature of the catalytic reaction is increased [408]. Spectroscopic

analysis of the surface after low-temperature olefin hydrogenation reactions has led to the identification of the irreversibly bound species as alkylidynes [248,600,639,795]. Additional indirect evidence has suggested that similar species may be present on the surface and may be direct intermediates in hydrogenolysis processes as well [626,739]. A molecular model of the working catalyst has been advanced based on these results where the surface is mostly coated with three-dimensional carbonaceous islands but still retains some patches of uncovered bare metal [796]. The demanding steps in hydrocarbon conversion reactions, which involve C–C bond scissions (isomerization, hydrogenolysis), probably occur on the exposed metal sites, but the initial and final hydrogenation–dehydrogenation steps are likely to be aided by the strongly adsorbed moieties. Those moieties not only passivate the metal surface, but also act as a reservoir of hydrogen atoms [290].

In order to understand the hydrogenation of unsaturated hydrocarbons, the formation of π -bonded olefins needs to be included in the mechanistic picture. By adsorbing on top of other chemisorbed species, these weakly bonded species act as extrinsic precursors. They are in principle different than the intrinsic intermediates to adsorption reported on clean platinum [313], but appear to display similar electronic and geometrical properties, as witnessed by the similarities between the infrared spectra of the π -bonded olefins under vacuum [229], and the infrared [633,795] and sum-frequency generation [600,797] data obtained under reaction conditions. Molecular beam work on the ethylene hydrogenation/Pt(1 1 1) system has revealed that: (1) weakly bonded olefins are indeed the ones that intervene directly in the hydrogenation process; (2) the dissociative adsorption of hydrogen on the surface is rate-limiting for the overall reaction; and (3) strongly adsorbed alkenes and other carbonaceous deposits inhibit the latter step [409].

Hydrogen plays a unique role in most hydrocarbon conversion processes. It has been long recognized that one of the key functions of metals as catalysts in hydrogenation–dehydrogenation and skeletal rearrangement reactions is to activate molecular hydrogen to produce chemisorbed hydrogen atoms [781]. However, the exact manner in which the resulting atomic hydrogen participates in the hydrocarbon conversion steps is not entirely understood yet. In particular, hydrogen addition must be intimately related to the presence of the carbonaceous deposits on the surface. It is clear that those do not intervene directly in the hydrogenation mechanism, since their own hydrogenation can be driven only at high temperatures [408,798], but they could help in the transfer of hydrogen from the surface to the olefin. Alternatively, they could just be spectators, their only role being as surface passivators. What is clear is that the presence of hydrogen in the reaction mixture significantly affects the selectivity of many reactions, not only of hydrogenation versus dehydrogenation, but of more complex reforming situations as well [249]. An elegant early example of this was reported by the group of Somorjai et al. in their study of the conversion of cyclohexene on Pt(1 1 1) over a 10 order-of-magnitude pressure range [627]. There, they showed that the selectivity of benzene (dehydrogenation) over cyclohexane (hydrogenation) production goes from a ratio of about 100:1 below 10^{-7} Torr total pressure to 1:100 at 10 Torr, even though the H_2 -to-cyclohexene ratio in the mixture of reactants was kept constant at a value of 10:1 at

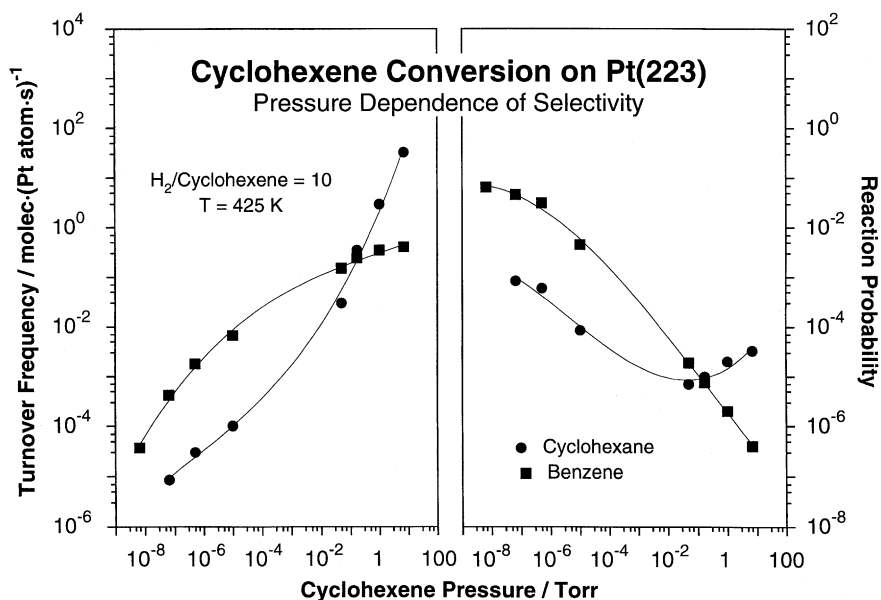


Fig. 23. Correlation between reaction rates (or, more accurately, turnover frequencies, left panel) and reaction probabilities (right) for the catalytic conversion of cyclohexene on platinum surfaces over a 10 order-of-magnitude pressure range. The reactions were performed at 425 K by using a stepped Pt(223) single crystal and gas mixtures with 10:1 hydrocarbon-to-hydrogen ratios [627]. There is a marked change in selectivity with pressure between hydrogenation reactions (cyclohexane formation), which dominate at high pressures, and dehydrogenation steps (benzene production), which prevail under vacuum. This is so even though the reaction mixture composition was kept constant in all experiments. Such behavior may be explained by the fact that the reaction probability changes in a more dramatic fashion for dehydrogenation steps due to their need for bigger platinum surface ensembles.

all pressures (Fig. 23) [627]. It was argued that this selectivity change is a reflection of an approximately constant reaction probability with changing pressure for hydrogenation, in contrast to the strong dependence of dehydrogenation rates on pressure due to the fact that those reactions require large surface ensembles of empty sites which become blocked by other adsorbates at high pressures. Similar conclusions have been reached in other studies.

Another issue relevant to real catalytic systems is that of the role of the structure of the surface in determining reactivity and selectivity. It was argued early in this review that surface bonding is quite localized (Section 2.1). In fact, some hydrocarbon species are believed to bond to one single metal surface atom. In that case, the surface chemistry is not expected to be very sensitive to the structure of the surface. On the other hand, many hydrogenolysis, isomerization, and other reforming reactions are known to require a reasonably large ensemble of atoms for their promotion. It is this distinction that has led to the identification of two types of hydrocarbon conversion catalytic processes, namely, surface-structure-insensitive and surface-structure-sensitive reactions [799,800]. While hydrogenation and dehy-

drogenation steps have often been considered to belong to the first category, the other more demanding reforming processes are known to be of the second type.

Studies on hydrocarbon conversion reactions with single crystals as a function of surface structure have led to some interesting observations [150,290]. For instance, the hydrogenation and dehydrogenation of most alkyls and alkenes appear to not depend strongly on the structure of the metal substrate. Under vacuum, ethylene converts to the same ethylidyne moiety on both (1 1 1) and (1 0 0) faces of rhodium and platinum [801], and most alkyl groups follow hydride and reductive elimination steps at about the same temperature on (1 0 0), (1 1 1), and (1 1 0) planes of the same metal [328,329]. This corroborates directly what has been long believed by the catalytic community. An exception to this is the case of ethylene dehydrogenation on nickel, which leads to the formation of vinyl on Ni(1 0 0) [731,802], acetylene on Ni(1 1 1) [803], and acetylide on Ni(1 1 0) [804]. Less details have been obtained on the reaction steps involved in hydrocarbon conversion on stepped and kink surfaces, but CO titration experiments have indicated that both adsorption and decomposition of hydrocarbons are generally preferred at defect sites, presumably because of the stronger bonds that take place on those atoms [3]. Much more work is needed on the microscopic details of reactions at defects.

The most clear examples of structure sensitivity in hydrocarbon conversion processes have been reported for catalytic studies with different single-crystal surfaces [290,628,629,805]. In the case of the conversion of cyclohexene on different platinum surface planes, it was found that not only the activity, but also the selectivity towards reforming processes, changes with surface structure [627]. Alkane aromatization and isomerization reactions are favored by square rather than hexagonal surface atom ensembles (Fig. 24) [629,630,806], and structural defects such as steps and kinks are detrimental to dehydrocyclization processes and favor hydrogenolysis instead [628,629]. With reference to the last point, a straightforward relationship between hydrogenolysis activity and bare (that is, not covered with carbonaceous deposits) metal site availability in steps and kinks was established directly via post-mortem CO titration experiments [807]. Unfortunately, not all observations from real systems can be accounted for by the catalytic work with single crystals [808], perhaps because the former systems involve the activity of the support (usually high-surface-area silica–aluminas), and also incorporate the use of additives.

An alternative approach to probing the nature of the surface atomic ensembles required for specific reactions is the use of a second inert element to selectively block adsorption sites. Sulfur, for instance, is well known to act as a poison in reforming processes, reducing the overall conversion rates, but also modifying the relative rates selectively in favor of the desirable cyclization and isomerization products at the expense of cracking [809]. Quite exciting results have been also obtained from experiments using gold and copper, where in some cases an enhancement in reactivity has been seen which can only be justified by a complex electronic effect [810,811]. Additional differences have been reported in systems where the second metal is alloyed instead of just deposited as an overlayer [812].

In terms of bimetallic surfaces, a combination of ensemble and electronic effects are observed even in the most simple reactions. For instance, the activity of

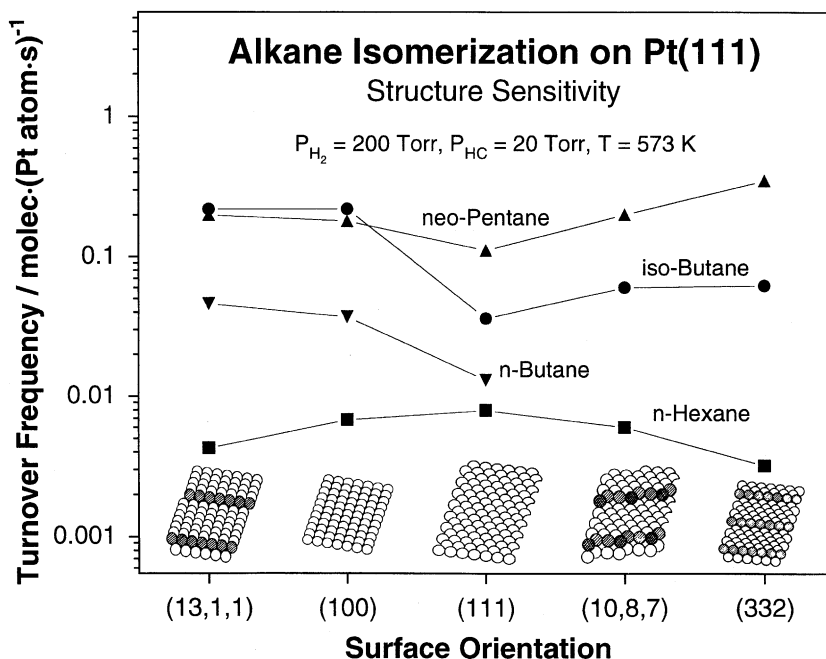


Fig. 24. Structure sensitivity in alkane isomerization reactions catalyzed over platinum single-crystal surfaces [628,629]. These studies allow for the direct correlation between activity and surface atomic ensembles. Notice, for instance, the significantly larger activity of (100) planes for *n*-butane and isobutane conversion, and the changes in reaction rates as steps and kinks are introduced in the surface.

platinum for the dehydrogenation of cyclohexene was found to actually be enhanced in absolute terms by the epitaxial deposition of one monolayer of gold [810]. There are also significant differences between epitaxial and alloyed systems, as proven by the study of the high-pressure catalytic conversion of *n*-hexane on Pt–Au systems: while epitaxially deposited gold poisons the sample for all reactions uniformly, alloyed surfaces proved to be particularly selective towards isomerization processes [812]. On the other hand, the addition of a more active and relevant second element to the platinum surface does not always lead by itself to the results observed in studies with supported catalysts. For instance, the addition of rhenium to platinum single crystals was seen to increase the selectivity towards the undesirable hydrogenolysis pathway [813,814]. Presumably, the C–C bond-breaking activity of rhenium needs to be moderated by the addition of sulfur to the reaction mixture to the point where the formation of lighter hydrocarbons is poisoned and the build-up of the carbonaceous layer is inhibited; under those conditions, the catalyst displays a particularly good selectivity for hydrocarbon reforming [815,816]. Finally, small amounts of potassium have been found to also poison the platinum crystals non-selectively, although more bare platinum atoms are available on the surface in that case [817].

8. New directions

It has been argued in this review that surface science has already contributed in significant ways to the understanding of heterogeneous catalysis. Perhaps its largest impact has been in the development of a general picture for the chemistry involved on the catalytic surface. That knowledge has underpinned the thinking behind the development of new catalysts and processes. The more we understand the microscopic details of surface reactions the less guesswork is required for the design of new processes. In particular, better-developed models for the surface–adsorbate chemical bond lead to a clearer definition of the catalytic problems. Kinetic and energetic measurements in model systems greatly advance our ideas on how to improve selectivities towards specific reactions. A better understanding of the structure and electronic properties of solid surfaces focuses the search for catalytic materials. Our progress in these directions is still incomplete, and is expected to continue in the next decades [26]. Below, a discussion is presented on a number of pressing unresolved issues in need of further study.

8.1. *Molecular manipulation and dynamics*

First, it is highly desirable to advance our understanding of the chemistry of surfaces from the atomic point of view. This requires a significant qualitative jump in the level of sophistication of the experimental techniques available, something that can be argued is already under way. In terms of the study of surface structure, surface bonding, and even chemical reactions at the atomic level, significant and exciting advances have recently come from the development of STM and AFM [818]. STM has already been widely used to map the structure of surfaces in many systems [31,452]. However, a serious roadblock to a wider application of this technique to catalytic problems has been its lack of chemical sensitivity. It needs to be remembered that STM typically maps surface electron density, not topography, and that the two are not always easy to correlate [103,819]. One solution to that problem is to perform spectroscopic determinations on specific positions of the surface via measurements of the tunneling current versus bias voltage. This is known as surface tunneling spectroscopy (STS), and both electronic [820] and vibrational [821] spectra of individual adsorbates can be obtained that way. STM studies have also begun to provide new information on the role of steps, kinks and other defects on the overall chemistry of surfaces [654,655,822]. It is even possible to actively manipulate individual adsorbates with the tip of a scanning probe, to the point of inducing specific chemical reactions on the surface [823]. For instance, Lauhon and Ho [570] have used electrons provided by the STM tip to induce dissociation, desorption and diffusion on single acetylene, pyridine, and benzene molecules adsorbed on Cu(001) via localized electronic and vibrational excitations. Perhaps more exciting is the report by Rieder and coworkers [824] on the manipulation of iodobenzene adsorbates on a copper surface to manufacture a biphenyl product; the images pertaining to the steps involved in that study are provided in Fig. 25. The use of scanning microscopy for the mapping and manipulation of

Surface Reactions Driven by STM

Phenyl Coupling on Cu(111)

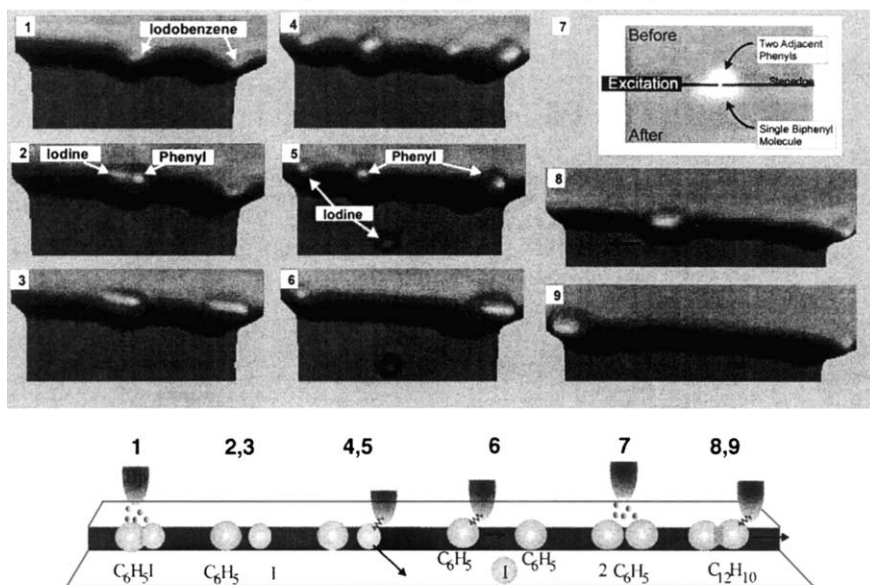


Fig. 25. Scanning tunneling microscopy may be used to manipulate surface reactions at the atomic level. This figure shows an example of this, a series of STM images illustrating the steps involved in a tip-induced Ullmann synthesis [824]. (1) Two iodobenzene molecules are adsorbed at a Cu(111) step edge. (2, 3) Iodine is abstracted from both molecules by using a voltage pulse. (4) Iodine atoms (small protrusions) and phenyl molecules (large balls) are separated by lateral manipulation. (5) The iodine atom located between the two phenyls is removed onto the lower terrace to clear the path between the two phenyls. (6) The left phenyl fragment is moved by the STM tip close to the right phenyl moiety to prepare for their association. (7) Electron excitation is used to fuse the two phenyl moieties into one biphenyl molecule. This panel shows a background-subtracted STM image with a phenyl couple in its center. The upper and lower parts correspond to the stages before and after the chemical association. (8, 9) Verification of successful chemical association. The synthesized biphenyl molecule is pulled by the STM tip across the image, from left to right. The bottom diagram offer a schematic representation of the whole process.

individual surface sites constitutes a particularly promising and exciting new direction in surface science.

From the point of view of dynamics, molecular beams can still be used in more sophisticated ways to map out the potential energy surface of adsorption–desorption phenomena. In particular, it would be useful to determine the mechanisms for state-to-state energy transfers between gas-phase molecules and solid surfaces. For instance, in a study with rotationally excited hydrogen molecules on Pd(111), it was shown that rotational excitation is possible even when the incident H_2 translational energy is less than the energy level spacing between the initial and final rotational states, indicating that part of the excitation energy originates from the surface, not solely from translational–rotational energy coupling [825]. More to the point, the

dissociative adsorption of H_2 molecules on $\text{Cu}(100)$ surfaces was found to not always be dominated by the site with the lowest potential barrier to reaction [826]. This means that by controlling the vibrational and collisional energy of the incident molecules one could in principle induce reaction at different surface sites selectively. These types of ideas require further testing.

Recent advances in laser technology have also yet to be fully exploited for the study of dynamics of surface reactions [563]. Pump–probe experiments in the picosecond–femtosecond time regime in particular could provide new insights into the nature of transition states. Some information has already been extracted from those kinds of experiments for energy transfer [563–565] and desorption processes [827], but virtually nothing has been done to apply ultrafast spectroscopy to the understanding of surface steps. Lasers could also be used to trigger specific surface reactions. Again, this idea has long been used to induce the fast desorption of adsorbates [470,476,542], but has seldom been employed to convert adsorbed species. This is not to say that there have not been studies on surface photochemistry, much work has indeed gone into trying to understand the dynamics of those processes (on distinguishing, for example, between direct and surface-mediated photodissociation steps [371,372]), but the full gamut of laser-based spectroscopic methods has not yet been utilized in this field. There is also the possibility of combining femtosecond laser pump–probe techniques with STM to study ultrafast dynamical phenomena on surfaces [828], or to induce specific chemical processes [829,830]. Recent efforts in femtosecond pulse-shaping and multiple-pulse femtosecond spectroscopy promise control over electronic and vibrational responses, and could ultimately be used to excite specific bonds in adsorbate species [831].

8.2. *Spectroscopy and kinetics*

At a mechanistic level, it is particularly important to be able to identify and characterize active reaction intermediates. As mentioned before, many intermediates adsorb only weakly on the surface, are present in small concentrations during reactions, and desorb readily upon removal of the reactants from the gas phase. All this makes their isolation under the controlled vacuum conditions typically needed for surface characterization almost impossible. Moreover, their detection needs to be achieved in the presence of large surface coverages of other adsorbed species. One of the most promising routes for studying these systems is to use optical spectroscopies in situ during the course of the catalytic reaction [63]. In that case, the attainment of surface sensitivity has to be achieved indirectly, via, for instance, the use of the unique spectroscopic features of the adsorbates, or by taking advantage of the reduced symmetry of interfaces, as in the recent studies of catalytic processes by RAIRS [62,795,832], non-linear optical spectroscopies such as second-harmonic and SFG [68,833,834], and nuclear magnetic resonance [835]. Additional discrimination of reaction intermediates from other strongly bonded surface moieties can be obtained by performing surface spectroscopic characterization experiments in a differential mode, via the induction of transients in the systems studied [26]. Optical spectroscopies can also address the study of solid–

liquid interfaces, but this area has barely received any attention to date [836,837]. Implementation of these ideas represents a great experimental challenge, but promises to deliver answers to some of the fundamental outstanding questions of catalysis.

Several new directions are also developing in connection with the quest for accurate kinetic measurements in catalysis. Present kinetic measurements on single crystals under catalytic conditions are often made by using micro-batch reactors, by transferring the sample between ultrahigh-vacuum chambers and high-pressure cells, and are reliable only within an order of magnitude. This is not sufficient to study small changes in reactivity with structure or other subtle effects. On the other hand, only for high turnover frequency reactions, of the order of unity, it is possible to simulate catalytic processes under more controlled vacuum conditions [393,428,487]. In terms of the use of molecular beams, one of the main limitations at this point is that there are currently no designs available for the generation of the high-flux beams needed to reproduce non-demanding reactions in their steady state [838]. Recall that in many instances the weakly adsorbed species believed to intervene in catalytic processes are short-lived, and likely to build up on the surface in detectable amounts only under the high-impinging-frequency condition that prevails in atmospheric pressure environments. One potential solution to this quandary is to design nano-liter-size reactors to attach to the surface of single-crystal surfaces under the well-controlled vacuum conditions of most surface-science experiments. In fact, related technology has been recently developed for the fast screening of miniature catalytic surfaces [839,840]. It is also conceivable to combine pulsed molecular beams with in-situ optical spectroscopies for the characterization of the chemistry of weakly adsorbed transient intermediates. Time resolution is also a possibility in those experiments; witness, for instance, the recent use of rapid-scan infrared spectroscopy for the study of the reaction of ammonia with oxygen on a platinum surface [841]. This technique, or even step-scanning infrared or Raman spectroscopies [842], could be used in kinetic studies under high pressures.

8.3. *Theory*

The development of a molecular-level picture of the chemistry that occurs at solid surfaces needs to also rely heavily on theoretical models and computer calculations. The meteoric increase in computer speed, capacity, and affordability in recent years has allowed for a corresponding rapid progress in computer methodology for calculations related to chemical systems. Certainly, computer modeling has gone from being a highly specialized field pursued by a handful of theoretical chemists to a widely available technique used by a large number of researchers. This general trend in chemistry and physics has also manifested itself in surface science. There are basically three levels at which computer modeling is being used to aid in the study of surface problems. At the atomic level, quantum-mechanics calculations are helping address issues related to chemical bonding, bonding geometry, spectroscopic transitions, and potential energy surface details. Molecular dynamics calculations are then employed to describe the evolution of microscopic phenomena within the

picosecond time regime. Finally, kinetic behavior is being emulated at a more macroscopic level with the help of Monte Carlo algorithms.

Atomic-level quantum-mechanics calculations are arguably the ones that have blossomed and developed to the largest extent in recent times [561]. That this is the case, in general, was recognized by the Nobel Committee in 1998 when it conferred the Nobel Prize in chemistry to Pople and Kohn. Ab-initio quantum-mechanics calculations are now commonplace in much of the organic and inorganic literature [843]. Wave-function-based calculations have also been used extensively in the past to describe certain adsorption systems, mostly by using cluster models [204–208]. Unfortunately, those calculations are quite time consuming, requiring computer times that depend exponentially on the size of the system. This represents a major limitation for the study of surfaces, because estimations on small clusters have shown to deviate significantly from known behavior on surfaces. Metal–metal bond lengths become highly distorted (they deviate significantly from bulk or surface known values), edge effects tend to play a dominant role in determining adsorption sites (adsorbates are often found to be the most stable at edge sites), and contributions from second and third layers are difficult to include in reduced-size clusters. It could be said that cluster calculations have in general fallen out of favor in the surface-science community [844,845].

Fortunately, a viable alternative has become available in the form of density functional theory (DFT) [846]. As the name implies, this represents a rigorous quantum-mechanical approach based on calculations of electron densities rather than electronic wave functions. Because density functional theory is capable of handling many-atom systems, it is ideally suited for surface studies [847]. On the negative side, DFT requires a considerable amount of empirical parameterization [848]. In order to perform DFT calculations, there is a need to choose not only an appropriate basis set, but also adequate pseudo-potentials. Moreover, two-electron interactions are not handled explicitly, but rather added afterwards. This has led to the development of a number of variations from the basic DFT method, from the simplest local density approximation (LDA) of the exchange-correlation energy functional, to the addition of generalized gradient approximations (GGA). At present, the principal limitation of DFT models is that there is no clear route for the convergence of different methods to the correct answer, as in the case of ab-initio calculations. In spite of that, much has been learned from recent calculations about surface systems.

Perhaps the widest use of DFT calculations has been for the determination of structural details on surface adsorbates. Fig. 26 displays an example of the type of results that can be obtained with this approach, in this case for the coadsorption of oxygen and carbon monoxide on Ru(0001) [849]. The atomic structures of four ordered coadsorbate phases, all of (2×2) periodicity but with differing CO:O atomic ratios, were calculated. An excellent agreement was found for two of those phases with experimental determinations using dynamical LEED intensity analysis. The atomic geometry of the third phase and the stability of a new (fourth) ordered mixed phase were predicted but have yet to be confirmed. Bonding energies can also be obtained with reasonable accuracy by DFT. King and coworkers [850] have tabu-

DFT Calculations of Electron Density ($n\text{O}+m\text{CO}$)/Ru(0001) (2×2) Structures

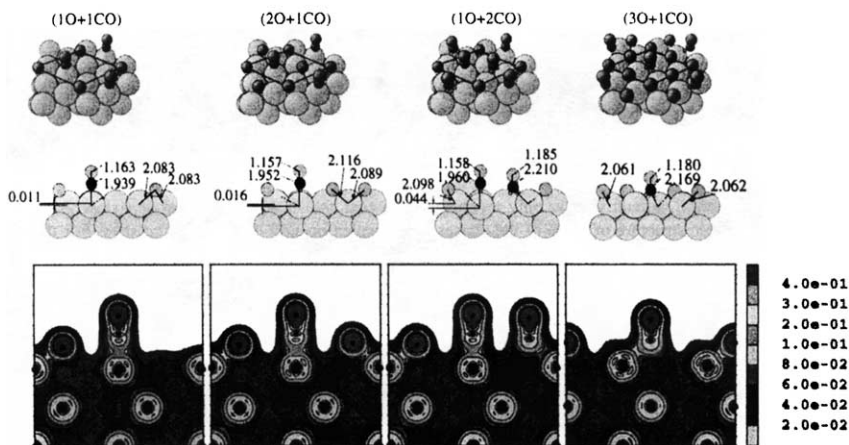


Fig. 26. DFT calculations of the electron density of the valence states of Ru(0001) surfaces with different coadsorbed O+CO (2×2) ordered structures [849]. Electron density contour lines are provided in electrons/bohr³, as in Fig. 2. The upper drawings show the adsorption geometries obtained by optimization of these systems, some of which have been corroborated by experimental LEED determinations. This example illustrates the level of complexity that can be studied in surface systems by state-of-the-art theoretical methods.

lated and systematically compared calculated versus measured heat of adsorption for simple molecules (CO, NO, O₂) on metals, and concluded that, in general, both agree to a better than a 10% error. Finally, spectroscopic data can be extracted from DFT calculations as well. For instance, the agreement obtained between the predicted vibrational spectrum and the experimental HREEL spectrum obtained from 2-iodoethanol on Ag(110) has been used to assign the surface intermediate formed in that system as an oxametallacycle [347]. In another example, the effect of coverage on vibrational frequencies and adsorption sites was probed for NO on Pd and Rh(111) [851]. NO was calculated to adsorb on the threefold fcc and hcp hollow sites, and to display vibrational frequencies between 1544 and 1643 cm⁻¹, in agreement with the HREELS and IR experimental values. This has brought into question the usual assignment of such vibrational modes to bridge adsorption.

Calculations of potential energy surfaces for surface reactions, or, at the very least, the discrimination among likely transition states, are somewhat harder, but still within reach. In one example, the chemical bonding aspects of the transition state structures for the dissociation of methane on Ru(0001) have been investigated [554]. Activation barriers for the sequential dehydrogenation steps were estimated to amount to 85 kJ/mol for methane decomposition, 49 kJ/mol for methyl conversion to methylene, 16 kJ/mol for the conversion of methylene to methylidyne, and 108 kJ/mol for the final dehydrogenation of CH(ads) to surface carbon [554]. In

terms of the effect of pressure on reactivity, experimental studies on the catalytic oxidation of CO on Ru(0001), have shown that, while high-pressure catalytic rates are the highest of any transition metal, under ultrahigh-vacuum conditions the rate is by far the lowest [852]. Theoretical modeling was used in this case to determine that the observed behavior is related to the fact that ruthenium can support high concentrations of oxygen on the surface, and that under those conditions the oxygen–metal bond is atypically weak compared to that at lower coverages [852]. In a third example, the effect of surface coverage on reactivity was explored for the adsorption and hydrogenation of ethylene to surface ethyl intermediate on Pd(111) [549]. At low coverages, di- σ adsorption of ethylene was calculated to be 32 kJ/mol stronger than the π adsorption mode, the intrinsic activation barrier for hydrogenation of di- σ ethylene was estimated at 88 kJ/mol, and no direct pathway for hydrogenation of π -bonded ethylene was identified. At higher coverages, on the other hand, lateral repulsive interactions between adsorbates destabilize the di- σ species, and a new stable configuration develops with π -bonded ethylene adsorbed next to a hydrogen atom in a neighboring bridge site, leading to hydrogenation with an intrinsic barrier of only 36 kJ/mol.

Overall, state-of-the-art DFT calculations of adsorption and reaction energies are usually within 5 kcal/mol of the experimental values, but activation barriers can be over-predicted by as much as 10 kcal/mol [853]. Highly exothermic reactions with small activation barriers, of the order of 2–5 kcal/mol, and/or involving hydrogens, are particularly difficult to reproduce [854]. Structural determinations are perhaps more reliable: it is relatively easy to determine bond distances and bond angles within accuracies of about ± 0.02 – 0.04 Å and ± 1 – 5° , respectively [855]. The alteration of adsorbate-surface bonding and surface reactivity by extrinsic effects such as substituent effects, bimetallic promotion, and transient surface precursors has also been investigated with theoretical models [853].

The next level of theoretical characterization of chemical reactivity is addressed by molecular dynamics. There, the static potential energy surfaces calculated with the quantum-mechanical methods described above are used to examine the dynamics of atomic and molecular adsorbates over time [847,856]. This can in principle be done by employing a full quantum-mechanics description of the motions of molecules on those potentials, but are often performed in the classical limit instead for reasons of economy. Even then, only phenomena occurring in time intervals of the order of a few picoseconds can be simulated with the present state-of-the-art computers and algorithms. This is sufficient to explore some dynamic problems related to the surfaces themselves such as vibrations and reconstructions, but represents a severe limitation when considering actual chemical reactions [857,858]. A few examples of the application of molecular dynamics to problems of catalysis do exist [859], but further advances in computer speed will be required before this approach makes a real impact on the study of catalysis.

Finally, macroscopic kinetics can be connected to microscopic surface phenomena via Monte Carlo (MC) simulations. MC algorithms are specially suited for this, because they start from a small representation of what the surface-adsorbate system is believed to look like. In that sense, this is a statistical method that approaches the

exact solution as the sampling size is increased. A formal stochastic derivation of the MC method for simulating chemical kinetics was provided in the 1970s by Gillespie and coworkers [860], and extended to non-homogeneous systems soon afterwards [861]. One of the advantageous features of MC methods for the study of surface systems is that, because they rely on the direct observation of temporal changes on a piece of the (simulated) surface, they are quite amenable to the inclusion of local effects such as adsorbate–adsorbate interactions and island formation [862]. In one application, MC simulations were used to study the effect of precursor mobility on the uptake of gases on surfaces [427,863]. It was found that the sticking coefficients obtained from the simulations are consistently lower than are those obtained by using the Kisliuk equation (Section 3.1) [423]. Two reasons were proposed to explain this discrepancy, namely, islanding of the adsorbates on the surface, and site revisiting in the precursor state [427,863]. MC methods also provide an easy way to visualize kinetic changes on the surface. This is particularly useful when trying to understand the effect of islanding or adsorbate diffusion on reaction rates [864]. Finally, site-dependent energy distributions with spatial correlations can also be easily incorporated [865]. MC simulations are expected to complement future isothermal surface reaction kinetic measurements of the type discussed in Sections 3.4 and 8.2.

Theoretical modeling is expected to play a more important role in catalysis understanding and development in the near future. In addition to the increasing use of each of the methods described above, the most likely new direction in this field may be the combination of simulations at different scales. For instance, a first-principles-based dynamic MC algorithm has been developed to simulate catalytic kinetics on well-defined transition-metal surface which incorporates density functional calculations to establish an intrinsic kinetic database [562]. Both pairwise and bond order conservation models are parameterized from this database and used internally in the MC simulation to describe adsorbate lateral interactions. Other examples have shown how to bridge different types of calculations to include phenomena over wide ranges of time and space [866,867].

8.4. Simulation of realistic systems

Most of the experimental advances discussed above address issues of fundamental chemistry and of bridging the pressure gap. A significant effort needs to be put into bridging the materials gap as well. In that context it can be said that, in the new emphasis being placed on nanotechnology within the last couple of years, catalysis is both an early contributor and a likely beneficiary. Most catalysts consist of an active phase finely dispersed in a high-surface-area support as small nanometer-scale particles. It has been long recognized that many problems associated with the activity and selectivity of catalysts have their root in the heterogeneity of the dispersed catalytic particles. It is therefore highly desirable to develop ways of preparing supported catalysts with particles of uniform size and shape in a reproducible manner. The revolution introduced by the use of crystalline supports such as zeolites in catalysis would be greatly surpassed by the achievement of this goal.

One of the early ideas in this direction involved the decomposition of organometallic clusters [868]. Unfortunately, that approach has proven only partially successful, mostly because the initial clusters tend to sinter (coalesce) during catalyst preparation. A newer procedure involving the use of colloids as precursors for the supported particles looks somewhat more promising [869–871]. Even though the colloidal approach does suffer from some of the same difficulties encountered in the organometallic method, the initial larger size of the colloidal particles makes them more likely to retain their size and shape after deposition and treatment. Narrow particle size distributions can be obtained, and average sizes can be controlled, by changing colloid preparation conditions [872,873]. In fact, even particle shapes can be changed in this manner. In one example, the shapes and sizes of Pt nanoparticles have been controlled by changes in the ratio of the concentration of the capping polymer material to the concentration of the platinum cations used in the reductive synthesis of colloidal particles in solution [874]. Preparation of particles with tetrahedral, cubic, irregular-prismatic, icosahedral, and cubo-octahedral shapes was possible this way. Bimetallic particles can be synthesized via colloids as well [875–877].

The advent of new nanolithography technologies promises to circumvent the problems associated with other chemical manufacturing procedures in surface-science studies [878,879]. Good model catalysts with periodic arrays of uniformly sized metal particles on high-density supports have been prepared this way [880], and their stability under reaction conditions has been probed [881]. It was seen, for instance, that under the catalytic reaction conditions used to oxidize hydrogen with oxygen ($T = 1000$ K, $P = 1$ atm), the original deposited platinum flat disks transform to three-dimensional particles. A few catalytic reactions have also been tested on these catalysts. For example, platinum model catalysts with particles 28 ± 2 nm in diameter deposited on a silica substrate displayed a factor of two higher activity than platinum foils for cyclohexene hydrogenation at 100°C [882]. In fact, the selectivity towards dehydrogenation was three times higher on the nanolithographic surface, while the rate of deactivation was about the same as for the Pt foil. It was speculated that the reason for those differences may be related to changes in the interface between the platinum particles and the silica support. At present, nanolithography can only carve features down to a few hundreds of angstroms, still too big to produce particles of relevance for most catalytic processes, but this limitation is likely to be overcome in the near future.

A recent and very exciting alternative for the preparation of monodispersed catalysts has been developed by Schneider and coworkers [883], where the deposition of mass-selected metal clusters with 1–30 atoms each is accomplished by using a sputtering source and a mass quadrupole filter. A couple of catalytic reactions have been tested on those systems so far. In one, a single palladium supported atom was shown to be sufficient to promote the conversion of acetylene to benzene, but a critical ensemble of seven atoms was proven necessary for high-temperature cyclo-trimerization (Fig. 27) [884]. In the case of CO oxidation on gold, it was concluded that the inert nature of the bulk metal breaks down when small particles are considered [885].

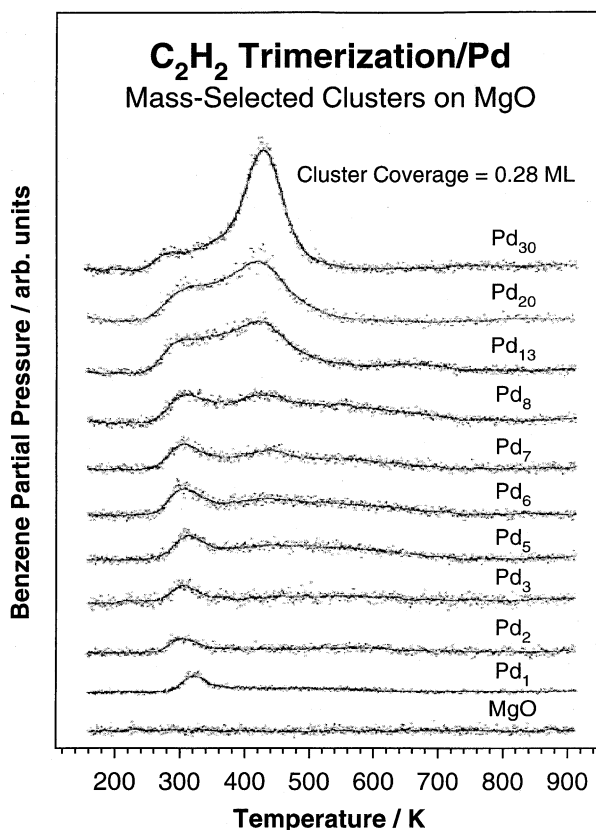


Fig. 27. Benzene TPD traces from acetylene trimerization on palladium clusters of varying sizes, from a single palladium atom to 30 Pd atom particles, deposited on MgO(1 0 0) [883]. The clusters were prepared by laser ablation, and mass filtered in the gas phase prior to deposition on the magnesium oxide surface. Their coverage was 0.28% ML in all cases, or 6.3×10^{14} atoms/cm². The bottom spectrum shows that no benzene is produced on clean MgO(1 0 0) films. Chemical conversion is seen with as little as one palladium atom per deposited particle, but a new high-temperature reaction channel opens up only for clusters with about seven atoms or more.

More realistic supported catalyst models have been prepared and characterized by well-established vapor deposition techniques. In particular, metal catalysts deposited on oxide supports have been emulated by the sequential physical deposition of thin oxide films and metal particles on well-defined refractive substrates [704,706,886]. In terms of the CO oxidation on gold process mentioned in the previous paragraph, catalysts with gold clusters 1–6 nm in diameter deposited on TiO₂ single-crystal surfaces were prepared and tested in ultrahigh vacuum in order to correlate physical properties with activity [887]. STM and reaction kinetics measurements showed that the structure sensitivity of this reaction on the gold clusters is related to a quantum size effect, with islands with two layers of gold being the most effective for catalysis

Au Particles Deposited on TiO₂(110) Electronic Properties versus Particle Size

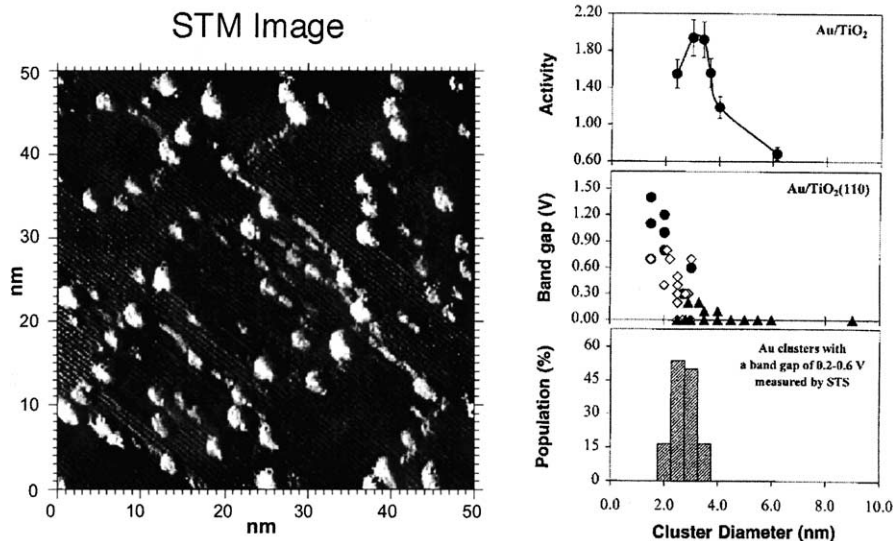


Fig. 28. It is now possible to combine scanning microscopy with catalytic measurements to establish structure–reactivity correlations and understand the physical properties responsible for changes in the behavior of catalysts with particle size. In this example, the activity of supported gold particles was tested and correlated with their electronic properties [887]. Left: Typical STM image of gold particles deposited by Au evaporation on a TiO₂(110)-(1 × 1) surface. Metal coverages of 0.25 ML were used in all cases. Right, top: Activity of the Au/TiO₂ system for CO oxidation at 350 K as a function of the Au cluster size. A 1:5 CO:O₂ mixture was used at a total pressure of 40 Torr. The activity is expressed in terms of turnover frequency (TOF = product molecules/(total Au atoms s)). Right, middle: Cluster band gap, measured by STS, again as a function of Au cluster size. Right, bottom: Size distribution of the Au clusters two atomic layers in height that exhibited a band gap of 0.2–0.6 V.

(Fig. 28). Studies where this methodology is applied to more demanding reactions are still in the future.

A more subtle aspect of the materials gap is that the initial structure and composition of the catalysts may not be retained under the conditions of the reactions. Indeed, the fact that solid surfaces reconstruct to minimize their surface tension has been recognized for some time [286]. Adsorbates in particular are known to not only induce surface structural changes, but also facilitate the segregation of specific components. It is therefore imperative to study catalytic surfaces *in situ* during the course of the reactions in order to characterize their active phase. This problem has barely been addressed to date. Changes in surface composition can sometimes be assessed by post-mortem analysis, but caution must be exerted when extrapolating those results to the description of the active catalyst because of the potential reversibility of the changes induced by the catalytic environment. Catalyst deactivation has been studied *in situ* by using electron microscopy [888]. It has been reported that,

in some cases, large filamentous carbon fibers grow during hydrocarbon conversion, and carry the catalytic metal particles away from the support. The structures of the metal surfaces themselves can also change dramatically when in the presence of high pressures of reactants, as recently suggested by in-situ STM experiments [707]. Again, work to answer these questions is yet to be done.

Finally, there have been some recent reports on an alternative approach for the formulation and testing of new catalytic materials and processes based on an extension of the idea of combinatorial chemistry [889]. A few research groups have in the past few years shown how the use of clever automated techniques such as IR thermography [890], resonance-enhanced multi-photon ionization [891], and differential mass spectroscopy [839] can be used for the rapid screening of large quantities of potential catalysts. A good example on how this approach works for fast catalyst screening is that of Liu et al. [892], who recently demonstrated how to prepare a 144-member catalyst library and to screen those for catalytic activity for the oxidative dehydrogenation of ethane to ethylene. For V–Al–Nb trimetallic oxide catalysts, Nb was found not to affect the catalytic activity of the V–Al oxides, in contrast to the effect of Nb seen in Mo–V–Nb oxides. For the Cr–Al–Nb oxide library, the most active catalyst contains only about 4% Nb, pointing to the fact that further composition mapping is necessary for the discovery of new heterogeneous catalysts in those ternary systems. In general, it is important to note that the optimum use of this “multiple-sample” approach still requires the good basic chemical understanding developed by the more standard studies discussed elsewhere in this review.

8.5. *New problems*

Surface-science research on catalytic problems is aimed not only at answering fundamental questions, but also at helping design new, more selective and more efficient, industrial processes. As stated in the introduction, catalysis is a mature field, and is already used in a large number of practical applications. Some future improvement in established processes such as petroleum refining and the production of many commodity chemicals is desirable, even if those are likely to be incremental. Yet other old systems still face fundamental difficulties in need of answers. For instance, there is still no viable process for the efficient conversion of carbon dioxide, in particular for its removal from the atmosphere [893]. It has also not been possible to successfully generalize the process for ethylene epoxidation to heavier olefins [894,895]. Outstanding problems in the synthesis of silicon-containing compounds, in hydrosilylation [896–898] and in the direct process for the synthesis of methyl chlorosilanes [696], for instance, have received little attention from the surface-science community. The controlled synthesis of polymers with specific molecular weight distribution and tacticity is still difficult. Note that even though most polymerization catalysts are based on organometallic complexes [899,900] (although some heterogeneous catalysts also exist for this [901,902]), they become heterogeneous as the polymer chains grow.

In addition, both the need for environmental remediation and the growing demand for new products continue to require new innovative processes. For instance,

heterogeneous catalysis promises to substitute many highly polluting stoichiometric organic synthesis processes in operation today [903,904]. New processes are continuously being demanded for the removal of pollutants from air [905] and water [906–908] sources. The heterogeneous reactions involved in atmospheric chemistry, such as the role of ice in catalyzing the formation of the ozone hole [909–912] and the role of sea particles in promoting the appearance of tropospheric smog [913], are poorly understood. A new generation of cheaper and more flexible catalysts are needed to replace the three-way catalyst presently used in automobiles and stationary power sources [914,915]. Catalysts are needed for the low-temperature oxidation of poisonous carbon monoxide [916]. An interesting new challenge is the development of catalysts for odor removal [917–919]. Permeable reactive barriers containing iron-based catalysts are an emerging alternative to traditional pump-and-treat systems for the removal of a large number of organic and inorganic contaminants from underground water [920,921]. Surface-science studies could greatly advance such new technologies.

Many other future problems are likely to be solvable using catalysis technology. Alternative energy sources will require creative catalytic processes, among others clean and small reforming reactors and efficient fuel cells [905,922,923]. Selective chemical sensors, many of which rely on catalytic processes, are in continuous demand [924]. The synthesis of chiral compounds is another growing field where heterogeneous catalysis could play an important role [836,925–929]. This list is by no means exhaustive.

9. Conclusion

In this review, the key issues associated with the surface chemistry of catalysis were surveyed. Particular emphasis was placed on identifying the contribution of modern surface-science studies to the field. As such, the review was limited mainly to the work performed with model systems and under controlled environments. In addition, it provided a personal and critical view of this area of research. The examples and the future outlook are far from comprehensive. A large fraction of this survey dealt with issues of basic chemistry, from discussions on the microscopic description of surface bonding and dynamics, through the identification of reaction intermediates and reaction mechanisms, to the extension of those concepts to more realistic catalytic conditions. The implication from this view is that perhaps one of the main contributions of surface science to catalysis has been to expand the basic knowledge needed for the improvement of existing processes and for the design of new ones.

Clearly, the empirical nature that the catalyst design process has displayed to date is minimized as we understand better the microscopic details of surface reactions. The gradual nature of this evolution often makes it hard to identify in short-term evaluations of the field. When taking a historic perspective, however, the contributions of surface science to catalysis become quite evident. For instance, an accurate description of the chemical bond allows for an easier visualization of the potential

problems in new catalytic processes. Accurate kinetic determinations are at the heart of understanding and improving the selectivity of heterogeneous reactions for practical applications. New, better, catalytic materials will evolve as the basic structural and electronic properties of solid surfaces are explained. And the field is still growing, so we can expect more advances towards solving the basic problems outlined in this review. The description of the surface–adsorbate chemical bond needs to be taken to the next level, one that better incorporates the role of neighboring surface atoms. Appropriate models for the kinetics of reactions in condensed matter systems, on surfaces in particular, need to be developed. The detection and characterization of direct catalytic surface intermediates has proven quite elusive, and needs to be pursued with renewed vigor. The preparation of complex surface models to better represent the processes that occur in real catalytic systems needs to be improved. We look forward to these future advances.

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