

Restructuring of Metal Surfaces and Adsorbed Monolayers During Chemisorption and Catalytic Reaction

BY G. A. SOMORJAI AND M. A. VAN HOVE

Department of Chemistry, University of California at Berkeley, and Materials Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA

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Abstract

The adsorption of atoms and molecules on crystalline metal surfaces frequently leads to restructuring of the metal surface. Such restructuring occurs during chemical reactions and is likely to profoundly modify the reactions. An overview of adsorbate-induced restructuring is presented, stressing the atomic-scale structural knowledge obtained on model single-crystal surfaces in ultrahigh vacuum with techniques such as low-energy electron diffraction *etc.*

1. Introduction

A considerable amount of information has been gathered over the years regarding the effect of adsorption and reactions on the surface structure of metal single crystals that are used as models for catalytic reactions and other surface processes (Somorjai, 1981; King, 1989; Somorjai & Van Hove, 1989; Somorjai, 1994a,b; Van Hove & Somorjai, 1994). The evidence points toward dynamic restructuring of the metal, in the form of geometric relaxations and reconstructions induced by the adsorbed atoms and molecules. As a result, the traditional view of a catalyst as a passive facilitator of chemical reactions has to be revised: the metal surface participates in reactions, by forming special (temporary) bonds to adsorbates as it restructures, even though the metal atoms are not consumed in the reaction.

We shall review major structural evidence for the active role of metal surfaces, as obtained from surface structural investigations (Watson, Van Hove & Hermann, 1993). Structural determination has developed to the point of providing much detailed information about 'adsorbate-induced restructuring', as we shall collectively name relaxations and reconstructions. Several techniques are used, foremost of which is low-energy electron diffraction (LEED). Considerable contributions also come from surface extended X-ray absorption fine structure (SEXAFS), photoelectron diffraction (PED), ion scattering at low, medium and high energies (LEIS, MEIS and HEIS) and X-ray diffraction (XRD), among other techniques.

Most studies in surface science and surface crystallography use model surfaces. These are either single crystals that are cut and polished properly along certain

crystallographic orientations, or evaporated thin films which are epitaxially grown as thin crystals on single crystal substrates. Ion bombardment, heating by electrical resistance and chemical methods are used to clean, smooth and order the crystal surfaces before deposition of selected atoms and molecules.

We shall refrain from referencing the voluminous original literature on the subject of this discussion. Instead, we refer the reader to the extensive lists of relevant publications contained in the related reviews by Somorjai & Van Hove (1989), Van Hove & Somorjai (1994) and Starke, Van Hove & Somorjai (1994), or in the structural database by Watson, Van Hove & Hermann (1993). Several useful historical overviews (written from the personal perspectives of the respective authors) can be found in the 1994 special volume (299/300) of *Surf. Sci.* entitled *The First Thirty Years*, edited by C. B. Duke: those accounts that are most relevant to our topic are listed in our publication list. Further useful overviews will be referenced below as appropriate. We will only reference explicitly original publications of relatively recent date.

2. Clean surface structures

2.1. Relaxation and reconstruction

Clean metal surfaces show atomic displacements near the surface: the atomic positions differ from the ideal extension of the bulk crystal due to the asymmetries introduced by the surface (Marcus, 1994). We talk of relaxations when these displacements are small compared with the interatomic distances, that is, generally smaller than *ca* 0.2 Å.

2.2. Relaxation

The most frequently observed type of relaxation is a change of the interlayer spacing between the two outermost atomic layers, relative to the bulk spacing. The topmost interlayer spacing usually is reduced, particularly on higher Miller-index surfaces of metals, which have a periodic terrace-and-step structure. Fig. 1 shows this effect on a clean platinum (210) crystal face. The atomic displacements are typically of the order 0.1–0.2 Å. Fig. 2 shows a compilation of data on how the relaxation

depends on surface roughness, which is defined as the inverse of the packing density in the surface plane (Jona & Marcus, 1988). The relative degree of contraction is larger the more open or rough the surface is. On low Miller-index surfaces, which are relatively close-packed, the spacing relaxation is either very slightly contracted or, in some cases, slightly expanded. Thus, Ni(111) and Cu(100) show no detectable relaxation, whereas Be(0001) (Davis, Hannon, Ray & Plummer, 1992) and Mg(0001) (Sprunger, Pohl, Davis & Plummer, 1993) exhibit expansions by *ca* 0.12 and 0.04 Å of the top-most interlayer spacing, respectively. This type of behavior for metal surfaces is well documented and can be made general (Jona & Marcus, 1988; Feibelman, 1994).

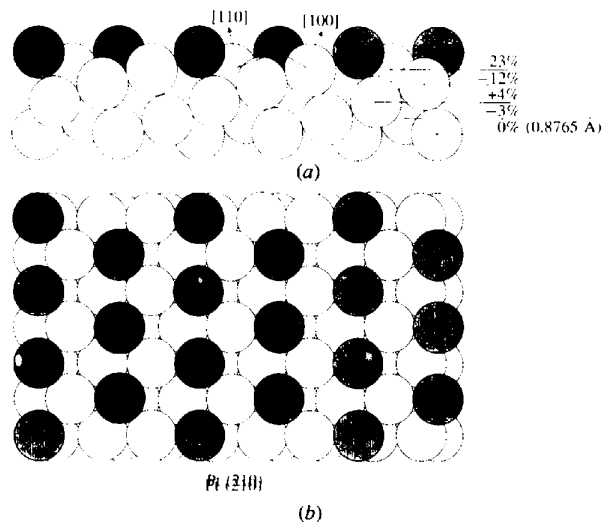


Fig. 1. (a) Side and (b) plan views of the Pt(210) stepped surface, exposing (110) oriented terraces and (100) oriented step faces. The outermost atoms are shown dark. Relaxations of interlayer spacings are marked as percentages of the bulk interlayer spacing (0.8765 Å), amounting to -0.20 ± 0.04 , -0.11 ± 0.05 , $+0.04 \pm 0.07$ and -0.03 ± 0.07 Å, respectively, with increasing depth.

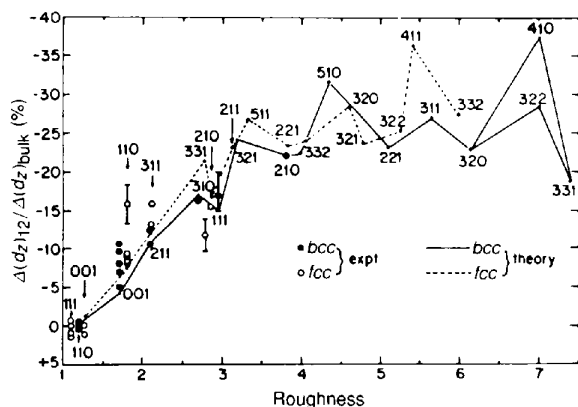


Fig. 2. Experimental and theoretical first-layer relaxation (in % of the bulk interlayer spacing) as a function of surface roughness (= 1/packing density) for several bcc and fcc surfaces. After Jona & Marcus (1988).

Also shown in Fig. 1 are relaxations of deeper interlayer spacings: these are detectable only for higher-index (stepped) surfaces. They often show sequences of contractions and expansions, that decay exponentially into the bulk over a depth of a few layers.

Lateral relaxations (parallel to the surface) are also seen for stepped surfaces, because of the lowered symmetry: an atom at a step edge has a different atomic neighborhood on its upper-terrace side than on its lower-terrace side, and generally prefers to move towards the upper terrace. These lateral relaxations have amplitudes similar to the interlayer spacing relaxations, and also propagate a few layers into the bulk.

2.3. Relaxation and reconstruction

Clean metal surfaces can also develop a nonbulk-like surface structure, through a more drastic process that is usually called reconstruction. Surface atoms are then displaced by an amount comparable to interatomic distances, such that bonds are broken and made. The result is a new phase that is limited to one or two surface layers. The first discoveries of surface reconstruction on metals occurred for iridium, platinum and gold (100) surfaces, shown in Fig. 3 (Heinz, 1994). In these surfaces the restructuring is due to the top-most surface atoms rearranging in a quasi-hexagonal, more close-packed configuration. The coincidence of positions in the top hexagonal layer and the underlying square unit cell gives rise to large coincidence cells, resulting in complex diffraction patterns. The (110) surfaces of the same Ir, Pt and Au undergo the so-called 'missing-row' reconstruction. In this circumstance, rows of atoms are missing and troughs are formed, also enlarging the two-dimensional unit cell, as shown in Fig. 4. The (100) surfaces of body-centered cubic metals are often reconstructed (Estrup, 1994). In these more open surfaces, there are enhanced opportunities for restructuring to optimize the atomic bonding.

To contrast metals with other materials, we first note that a majority of semiconductor surfaces reconstruct, often in complex manners, unlike the majority of metal surfaces which only relax. A relatively simple example is that of Si(100), illustrated in Fig. 5, in which pairs of surface atoms bond into 'dimers' to reduce the number of 'dangling bonds' left by the surface cut. Whether reconstructed or not, both semiconductor surfaces (Kahn, 1994) and polar ionic surfaces often exhibit large relaxations of individual atoms, on the scale up to *ca* 0.5 Å, e.g. for Fe₃O₄(111) (Weiss, Barbieri, Van Hove & Somorjai, 1993). This reflects the effect of the more directional covalent bonds in semiconductors, and of the strong electrostatic bonding forces in ionic surfaces. Nonpolar ionic surfaces, however, show little relaxation, presumably due to their charge neutrality. Examples are the MgO, NiO, CaO and CoO(100) surfaces (all of NaCl type).

3. Structure of adsorbate-covered surfaces

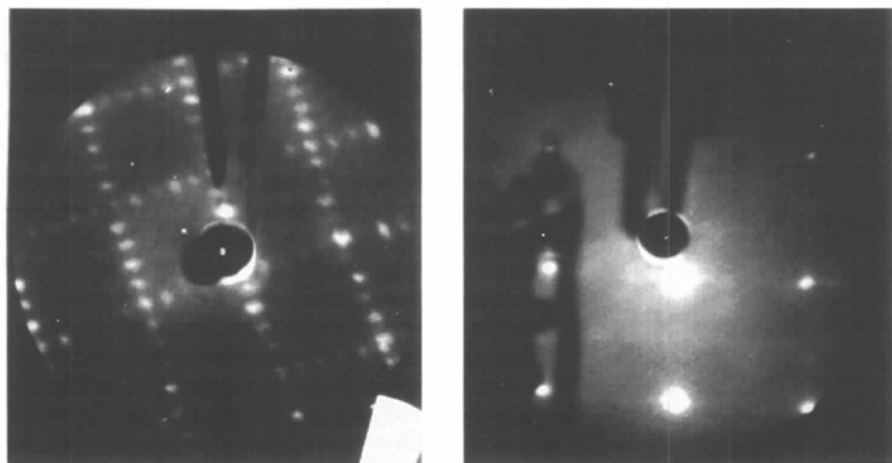
As we have seen, clean metal surfaces exhibit relaxations and reconstructions, relative to the bulk structure. Similarly, one expects and observes a new set of relaxations and reconstructions when a clean surface is covered with an adsorbate, whether it be an atom or a molecule. We shall here first mention a few easily observed examples of large-scale adsorbate-induced reconstructions, before turning to more detailed studies of both relaxations and reconstructions.

3.1. Qualitative studies of adsorbate-induced reconstruction

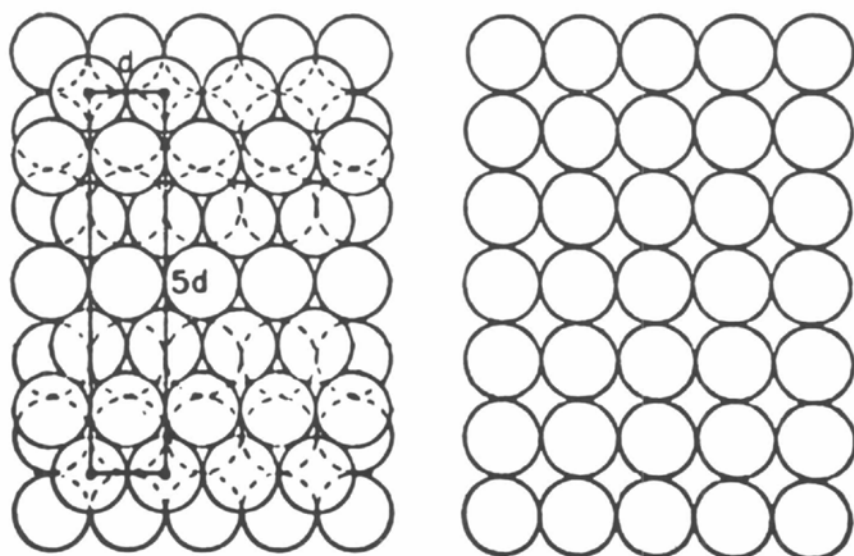
When adsorbates are placed on clean metal surfaces, the restructuring can become dramatic and dominant. First, let us review how adsorbate-induced restructur-

ing has been observed from qualitative surface science studies.

Fig. 6 shows the stereographic triangle for face-centered cubic structures that displays together surfaces with low and high Miller indices. The corners of the triangle represent the low-Miller index surfaces of the highest planar density. The sides of the triangle represent stepped surfaces, while the inside of the triangle corresponds to kinked surfaces (surfaces with steps which in turn also have periodic step-like notches). Clean stepped and kinked metal surfaces often adopt steps and kinks of single-atom height. When over 25 different crystal faces of platinum were heated in the presence of oxygen or of hydrocarbons that deposited a monolayer of graphitic carbon, restructuring of these surfaces was observed, with respect to their structure when clean. In oxygen the restructuring was of one type; in the presence of



(a)



(b)

Fig. 3. (a) Low-energy electron diffraction patterns and (b) structural models for *fcc*(100) surfaces, unreconstructed to the right, reconstructed to the left. A coincidence unit cell is drawn for the case of Ir(100)-(1 × 5), with a fivefold increase of one side of the unreconstructed square cell. The reconstruction can occur equally in two orthogonal directions on separate parts of the surface, giving rise to a diffraction pattern showing two domain orientations. The diffraction spots, which were photographed for Pt(100), exhibit splittings: these are due to a slightly distorted coincidence lattice as a result of slightly different lattice constants and a small rotation of the quasi-hexagonal reconstructed layer on Pt(100).

a monolayer of carbon it was of a different type. The nature of restructuring most commonly observed is a doubling or tripling of the step height with respect to that of the clean surface. In many cases one observes faceting (that is, new crystal planes develop) in the presence of a monolayer of oxygen or carbon.

Another example of adsorbate-induced restructuring is graphically shown by field ion microscopy, *cf.* Fig. 7. An almost hemispherical rhodium tip is imaged in the top panel of Fig. 7, exhibiting many crystallographic faces. When the rhodium tip is heated in carbon monoxide at

relatively high pressures, all the crystal faces restructure except the center (100) face, as seen in the bottom panel. When the carbon monoxide is desorbed and the surface is heated in vacuum, the original surface structure reappears.

Similarly, scanning tunneling microscopy studies carried out at high gas pressures show massive restructuring of the Pt(110) surface when the surface is heated in hydrogen, oxygen or carbon monoxide, as shown in Fig. 8. In hydrogen a 'missing-row' surface structure is generated. When heated in oxygen, large facets grow with new crystallographic orientations. When heated in carbon monoxide the surfaces become atomically smooth in between very high steps. On exchanging one gas for another, the respective surface structures are regenerated.

We have studied the molybdenum-sulfur phase diagram (Dunphy *et al.*, 1993): changes in the structure of various molybdenum surfaces with different step densities were observed as a function of sulfur coverage (*i.e.* two-dimensional density). The steps pair up, and double or become multiple in height. There is faceting at the surface. There are many ordered sulfur structures. In short, there are dramatic rearrangements of all molybdenum surfaces in the presence of one monolayer of chemisorbed sulfur.

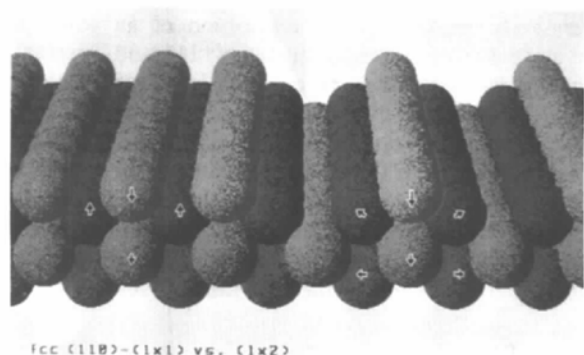


Fig. 4. Perspective view of $fcc(110)$ surfaces, unreconstructed to the left and reconstructed to the right with 'missing rows' of surface atoms. The missing rows expose deeper atoms and form more closely packed facets of (111) orientation. Similar reconstructions with deeper missing rows have also been observed, exposing wider (111) facets.

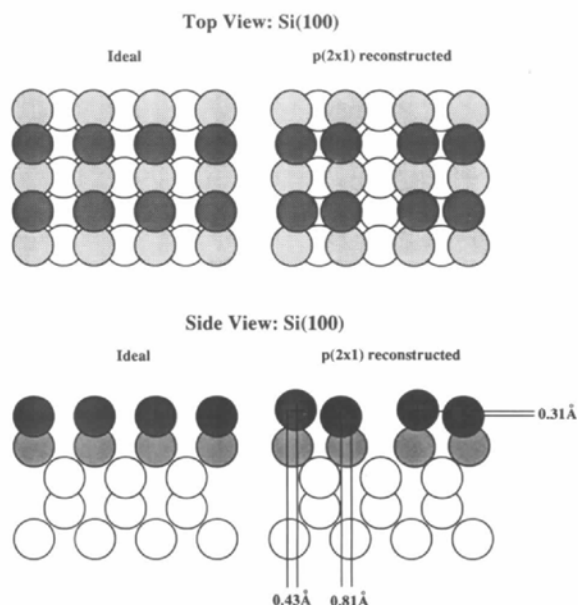


Fig. 5. Top and side views of $Si(100)$, unreconstructed on the left and reconstructed on the right. The darkest atoms are at the surface and provide two 'dangling bonds' each if unreconstructed. By pairwise bonding of the surface atoms, as shown at right, half of these dangling bonds are satisfied.

3.2. Quantitative studies of adsorbate-induced relaxation

In the last few years it has become abundantly clear that every time an adsorbate is deposited on a metal surface, substrate atoms near the surface are displaced by amounts ranging up to *ca* 0.2 Å (Starke, Van Hove & Somorjai, 1994). Such displacements are often comparable to and sometimes larger than the clean-surface relaxations, and they frequently point in the opposite direction, thus reversing clean-surface relaxations, sometimes even turning contractions into expansions.

Most obvious is a trend found when an adsorbate forms an overlayer outside the metal surface, rather than penetrating below the surface. Such adsorbates

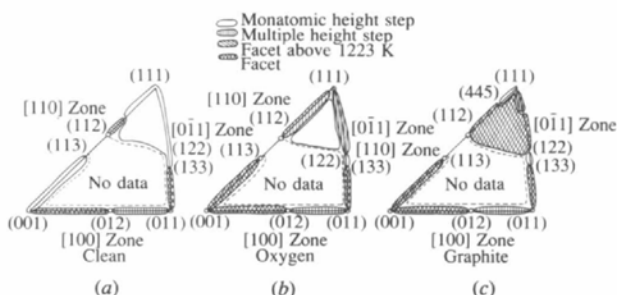


Fig. 6. Stereographic triangle for Pt surfaces, studied with a variety of exposed surface orientations. The occurrence of steps of mono-atomic and multi-atomic height as well as faceting, for (a) the clean surface, (b) the oxygen-covered surface and (c) the carbon-covered surface is shown.

systematically pull their metallic bonding partners outward from the surface. This effect reverses the clean-surface contraction of the top-most interlayer surface, by restoring part of the 'missing' bonds due to the creation of the surface from the bulk lattice. As an example, a S atom at low coverages on the (0001) face of rhenium bonds equally to three Re atoms, all of which are raised above the nonsulfur-bonded Re atoms, by a distance of *ca* 0.05 Å, as shown in Fig. 9. The same effect is seen with molecular adsorption, such as with carbon monoxide on Ru(0001) (Over *et al.*, 1992), and with ethylidyne on Rh(111) or Pt(111) (Barbieri, Van Hove & Somorjai, 1994a).

In more complex cases, one observes that the amount of such outward relaxation is governed by the adsorbate-substrate bond strength and by the number of such bonds. Thus, a high-coverage structure of sulfur on Re(0001), shown in Fig. 10, induces an unusually large buckling (Barbieri *et al.*, 1994). This occurs in the center of sulfur hexamer rings, where Re atoms are bonded to two S atoms simultaneously, as well as to two other raised Re atoms: there is a concentration of outward force within the sulfur rings. In another instance, when both benzene and carbon monoxide are adsorbed

in a mixed layer on Rh(111), the benzene bonds more strongly to the metal and pulls its metal bonding partners outward more than does the CO. The effect is reduced on Pd(111), to which the benzene adsorbs more weakly (Barbieri, Van Hove & Somorjai, 1994b).

As a rule, therefore, the outermost metal layer of low Miller-index surfaces is buckled by adsorption, with a buckling amplitude of the order 0.1 Å. An obvious exception to buckling occurs for high-coverage adsorption, where all metal surface atoms are equally bonded to adsorbate atoms and are thus equally pulled out from the substrate, leaving the metal layer planar. This is frequently observed.

The second metal layer below the surface is also frequently relaxed due to adsorption of an overlayer. In close-packed surfaces, like *fcc*(111) and *hcp*(0001) (*cf.* Fig. 9), this relaxation can simply be pictured as an elastic response to the relaxation in the outermost metal layer. Thus, when outermost metal atoms move outward, they exert outward forces on the atoms in the next layer down, thus causing a corresponding buckling there. Also, the buckling amplitude in the second metal layer will be roughly proportional to the number of bonds stretched outward by buckling in the first metal layer.

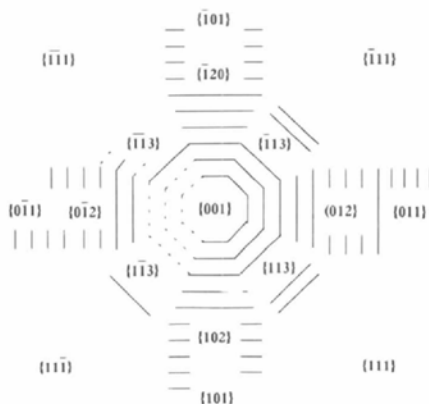
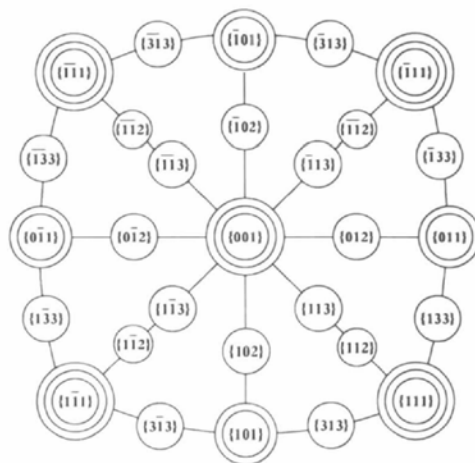
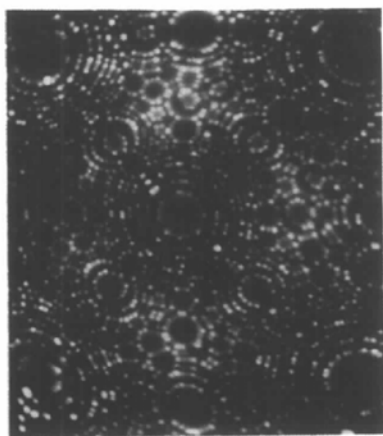


Fig. 7. Field-ion micrographs of a (001)-oriented Rh tip before (top left) and after (bottom left) reaction with 10^{-4} Pa of carbon monoxide during 30 min at 420 K (Gaussmann & Kruse, 1993).

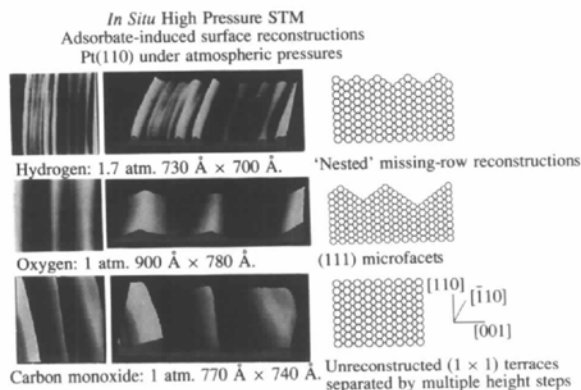


Fig. 8. Scanning tunneling microscope images of Pt(110) exposed to high pressures of hydrogen (top), oxygen (middle) and carbon monoxide (bottom). The left-most panels show plan views, the center panels perspective views and the right panels atomic models. The gray scale corresponds to height. The two-dimensional scan dimensions are indicated (McIntyre, Salmeron & Somorjai, 1993).

However, for less close-packed surfaces, such as *fcc*(100) and *bcc*(100), the picture is more ambiguous as far as the second metal layer is concerned (Starke, Van Hove & Somorjai, 1994). In some cases, the metal atom below the adsorbate in the second metal layer is pulled outwards (toward the adsorbate), as for carbon and potassium on Ni(100) and sulfur on Rh(100). In other cases, the opposite occurs, *i.e.* the metal atom is instead pushed deeper, as for oxygen and sulfur on Ni(100), nitrogen, chlorine and sulfur on Cu(100), sulfur and carbon on Mo(100) and sulfur on Cr(100). In the absence of a clear trend, an explanation for this divergent behavior is certainly needed: total-energy calculations are required to explain these effects. A possibly important quantity in this regard is lateral relaxations, which also affect bond lengths between the first and second metal layers: we discuss these next.

There are several cases where relaxations parallel to the surface have been detected. An early and most striking example is the adsorption of carbon on Ni(100) at a half-monolayer coverage, illustrated in Fig. 11. The carbon is small enough to penetrate deep into a hollow in the top-metal layer and bond directly to the second metal layer. This penetration is accompanied by a lateral expansion of the hollow site, which is accomplished by a rotation of the four neighboring metal atoms about the

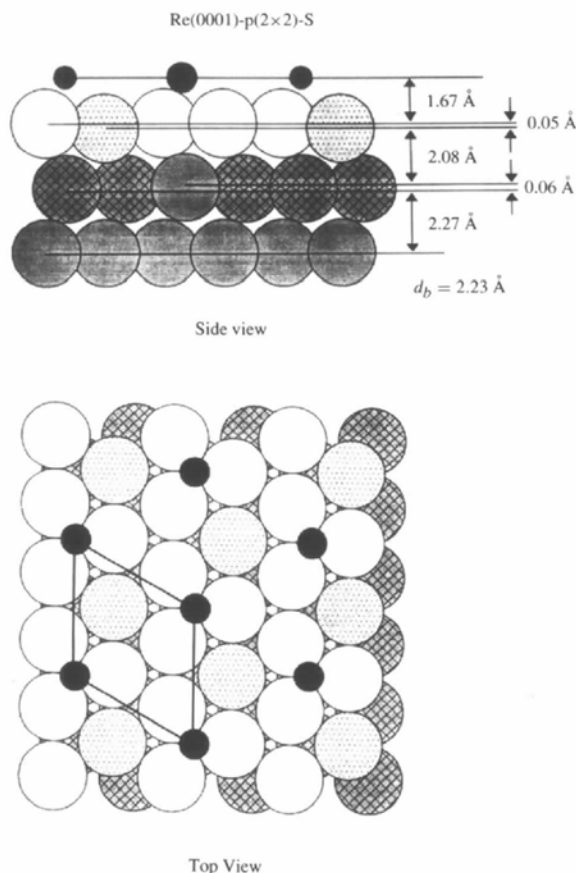


Fig. 9. Sulfur adsorption structure at low coverage (1/4 monolayer) on Re(0001), in side and top views. S atoms are drawn small and black, Re atoms large. In the top-metal layer, the white Re atoms (*i.e.* those bonded to S atoms) are raised above the light gray ones. In the second metal layer, the uniform gray Re atoms (which are directly below S atoms) are raised above the cross-hatched ones, being pulled up by the white Re atoms above (Barbieri *et al.*, 1994).

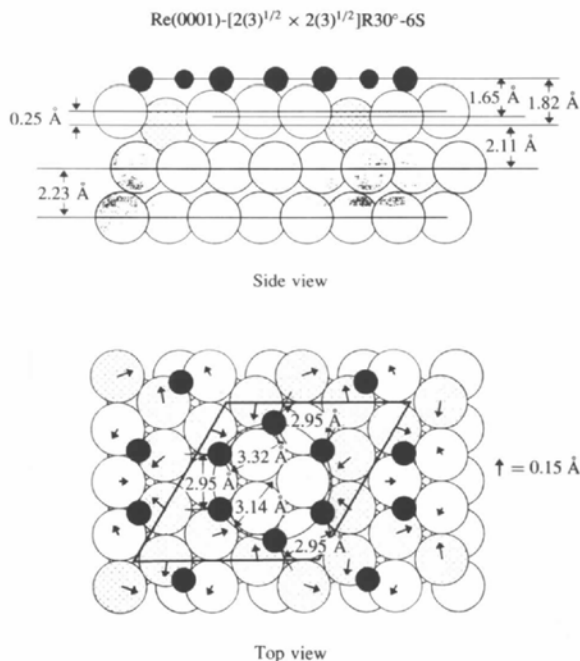


Fig. 10. High-coverage (1/2 monolayer) structure of S on Re(0001), in side and top views. S atoms are drawn small and black, Re atoms large. The top Re layer is buckled into a volcano shape: the white Re atoms form craters, being pulled high (0.25 Å) above the cross-hatched Re atoms, with dotted Re atoms forming the volcano slopes. Possible relaxations in the second metal layer were not examined. Note the repulsion between close-packed sulfurs, which are displaced away from the centers of threefold hollow sites (Barbieri *et al.*, 1994).

surface normal by *ca* 0.5 Å. New Ni—Ni bonds may be formed by this large relaxation, such that this case could qualify as a reconstruction, in our language. A more recent result concerns oxygen on Rh(110), shown in Fig. 12. The zigzag arrangement of oxygens on the surface induces a corresponding zigzag relaxation of Rh atoms in the second metal layer.

In many of these examples of relaxations, we see that an outward displacement of outermost metal atoms systematically gives rise to an expansion of deeper metal-metal bonds. We shall return to this important point.

3.3. Quantitative studies of adsorbate-induced reconstruction

As already mentioned, adsorbates can induce more drastic reconstructions in metal surfaces, involving bond breaking and making, relative to the ideal bulk termination. We next discuss selected examples of reconstructions for which the detailed surface structure is known.

A first type of adsorbate-induced reconstruction occurs typically at low adsorbate coverages and produces structures known already on clean surfaces. The case of alkali adsorption on Cu, Pd and Ag(110) (Nørskov, 1994) illustrates this behavior. A coverage of a few per cent of a monolayer causes the missing-row reconstruction to appear on these surfaces (which is illustrated in Fig. 4); this reconstruction is known on other clean surfaces (Ir, Pt and Au). Since such a low coverage is sufficient to induce the transition, clearly the reconstruction is a slightly metastable state of the clean surface itself for Cu, Pd and Ag(110). In some cases it may take a large coverage to achieve the same result, as for oxygen on Rh(110), where a half monolayer

of oxygen is required to induce the same missing-row structure (Comicioli *et al.*, 1993).

A new type of reconstruction can also be induced, for instance with oxygen adsorption on Ni and Cu(110), *cf.* Fig. 13. Here a different kind of missing-row structure occurs, accompanied by the formation of strings of alternating oxygen and metal atoms, as illustrated in Fig. 13. A related structure is formed by oxygen on Cu(100), which also exhibits missing Cu rows and strings of Cu and O atoms.

It is also possible for an adsorbate to remove a clean-surface reconstruction. This happens with oxygen on Ir(110), where the missing-row reconstruction of the clean surface is lifted in favor of the simple bulk termination, on which the oxygen atoms rest.

Of course, relaxations on the scale 0.1 Å are also generally present at reconstructed surfaces, just as they are at unreconstructed surfaces.

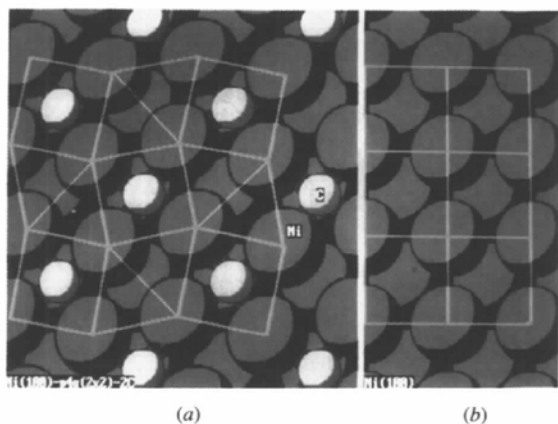
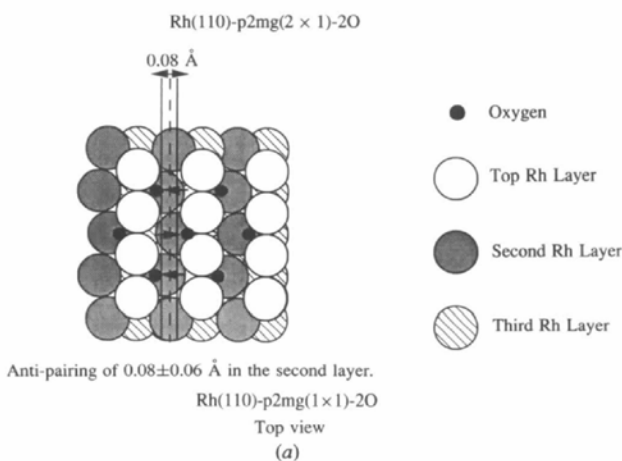


Fig. 11. (a) Carbon adsorption structure on Ni(100) at 1/2 monolayer: Ni(100)-p4g(2 × 2)-2C. For comparison, the clean Ni(100) surface is shown in (b). The C atoms are closer to the Ni atoms in the second metal layer than to those in the first metal layer. The clockwise/anticlockwise rotation is emphasized by the rotated and somewhat expanded squares.

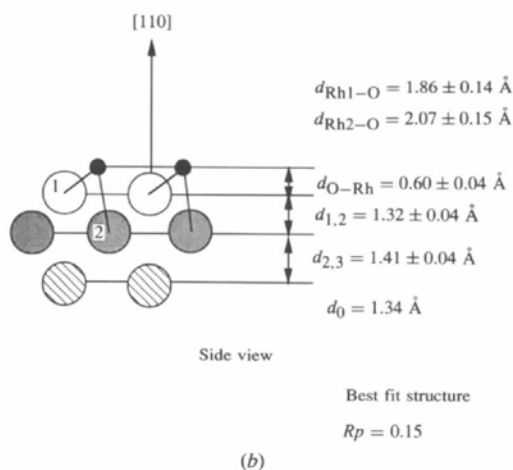


Fig. 12. Structure of a full monolayer of oxygen on Rh(110): (a) top view; (b) side view. Each oxygen bonds most closely to Rh atoms in the first metal layer, and less closely to the second metal layer, which undergoes a symmetry-allowed lateral zigzag distortion (Gierer *et al.*, 1993; Batteas, Barbieri, Starkey, Van Hove & Somorjai, 1995).

3.4. The flexible surface

All of these results oblige us to reassess the nature of the atomic model of solid surfaces that we use to try to understand various surface phenomena. Since the 1950s we have used the adatom-step-kink model, that is the rigid lattice model of rough surfaces, as a guide to surface phenomena (*cf.* Fig. 14). In this model it is assumed that the surface has atoms that are differentiated only by their number of nearest neighbors. There are adatoms, vacant sites, steps and kinks on surfaces. Each atom is assumed to sit in an equilibrium position that can be obtained by the projection of the bulk lattice to that surface. As we have learned from surface crystallographic studies, and exposed above, the metal atoms on clean metal and adsorbate-covered metal surfaces certainly are not located in their bulk-like equilibrium positions. They move downward, sideways, up, depending on the nature of the chemisorption bond. That is, surface atoms are flexible. They relocate to optimize their bonding to the neighboring atoms.

Therefore, it is much more realistic to speak of a flexible surface. The metal atoms in low Miller-index, high-density surfaces are bound by many nearest neighbors. When adsorption occurs, they may move up, down or slightly sideways, but they are fairly rigid

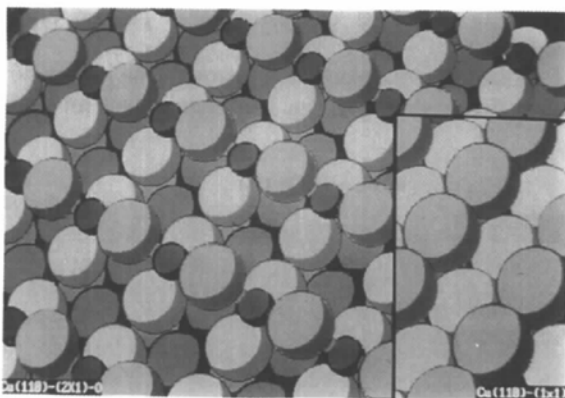


Fig. 13. Oxygen-induced reconstruction of Cu(110) at a coverage of $1/2$ monolayer. The inset shows close-packed atomic rows on the clean surface. These rows are broken up by the loss of every other metal atom, while oxygen cross-bridges the remaining metal atoms in the direction perpendicular to the original rows, thus forming —Cu—O—Cu—O— chains.

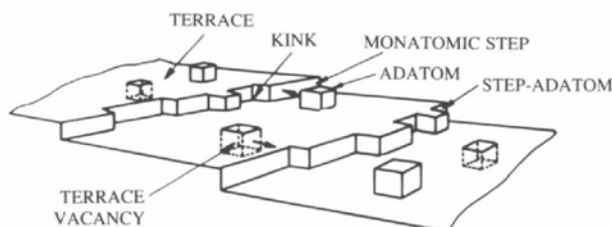


Fig. 14. Rigid-lattice model of a surface, composed of terraces, steps, kinks, adatoms and vacancies in bulk positions.

because the coordination shell keeps them in place. When the coordination is lowered, such as on surfaces with higher Miller indices (*cf.* Fig. 15), the act of chemisorption may more easily move the atoms outward because the exothermic chemisorption process can pay for the endothermic weakening of next nearest neighbor metal-metal bonds, since in this circumstance there are fewer bonds. Of course, at a step and even more so at a kink there are even fewer nearest neighbors, so step atoms can relax inward or outward more readily. The surface then looks more like isolated clusters, which are the most flexible because in this circumstance each metal atom has the least number of nearest neighbors. Therefore, the act of chemisorption can readily restructure the cluster, because the formation of a stable chemisorption bond can readily pay for the weakening of the few next-nearest neighbor metal bonds.

4. Surface phenomena that can be explained by adsorbate-induced restructuring

4.1. Cluster-like bonding at surfaces

Photoemission studies in several laboratories have revealed that the electronic structure of chemisorbed molecules is very similar to that in organometallic or carbonyl clusters. Similar results were found from vibrational spectroscopy studies of many organic monolayers on metal surfaces. The vibrational spectrum of small hydrocarbons on surfaces is very similar to that for organometallic clusters, which can be prepared readily

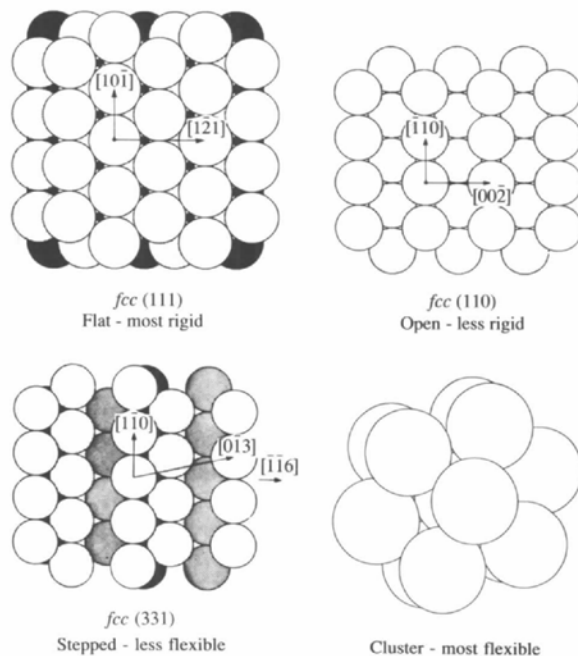


Fig. 15. Hierarchy of metal surfaces from mostly flat and rigid to mostly open and flexible. Atoms on open surfaces have more space to relax and reconstruct.

in a crystalline form and studied by IR spectroscopy. In fact, the vibrational spectra of organometallic clusters available in the literature have been used as a reference to identify the bonding of several surface species. Recently, organometallic chemists could also use the surface science literature to look for vibrational spectra that can be used to reference newly found organometallic cluster structures.

4.2. Rough surfaces do chemistry

A series of studies by Ibach and his coworkers (Lehwald & Ibach, 1979) indicated that the decomposition of ethylene occurs along similar chemical paths on the Ni(111), (110) and stepped nickel crystal faces. Ethylene dehydrogenates to acetylene and decomposes further to form carbon and hydrogen. However, the temperatures at which these decomposition steps occur are very different. At a stepped surface it is much lower (<150 K), while on the flat low Miller-index surfaces dehydrogenation occurs at or above 220 K. Thus, the stepped surface is much more chemically active in this reaction.

Molecular-beam scattering studies of H₂/D₂ exchange from platinum surfaces reveal that the reaction probability is almost unity on stepped surfaces (Lin & Somorjai, 1984). However, on flat defect-free surfaces, it is below the detection limit. These results clearly show that defects in these platinum surfaces, namely steps, are responsible for breaking H—H bonds.

4.3. Thermal activation of bond breaking

One of the most dominating phenomena in surface chemistry is the sequential bond breaking process that occurs with every chemisorbed molecule on every surface as the temperature rises. With hydrocarbon molecules, such thermal decomposition normally exhibits individual dissociation events that occur at well separated increasing temperatures. Each surface with a given structure thermally decomposes the chemisorbed molecules sequentially. The sequence is very well defined, and the temperature ranges within which certain fragments are stable are also well established.

It is very difficult to understand why such decomposition occurs in sequence rather than at once. One explanation is that of adsorbate-induced restructuring; a restructuring may occur as perhaps a first-order phase transformation at a given temperature. The relocation of metal atoms breaks symmetries in molecular orbitals of organic molecules, thereby causing bonds to break. There is need for experimental evidence to explore and correlate restructuring of surfaces with sequential bond breaking.

4.4. Coverage dependence of bonding

Among the most detailed studies of coverage dependence of adsorbate-induced restructuring were carried

out for hydrogen on the Rh(110) face (Heinz *et al.*, 1991). This system shows a continuous expansion of the outermost metal-metal interlayer spacing as the hydrogen coverage increases. In Figs. 9 and 10, we saw a further example of increasing relaxation with coverage. Another coverage-dependent study examined several structures of sulfur on Mo(100) and again found increasing relaxations with increasing coverage (Jentz *et al.*, 1995). To generalize: the higher the coverage the more the metal atoms will move from their equilibrium positions on the clean metal surface.

4.5. Coadsorption

We have seen above, with the example of coadsorbed benzene and carbon monoxide on the Rh(111) and Pd(111) surfaces, how the adsorbate-substrate bond strength affects the amount of relaxation induced in the substrate. Another aspect of these structures is that the benzene is a charge donor to the metal, while the CO is an acceptor under these conditions. The question one asks is whether the donor or acceptor nature of the adsorbate also affects the relaxation. Future studies will allow us to answer this important question of coadsorption-induced restructuring. However, those few studies that have been carried out to date indicate that the nature of metal restructuring under coadsorption conditions may be very different from that which occurs when only one type of adsorbate is present on the surface.

Coadsorption can also cause restructuring in a massive way, as demonstrated in Fig. 16. When carbon monoxide

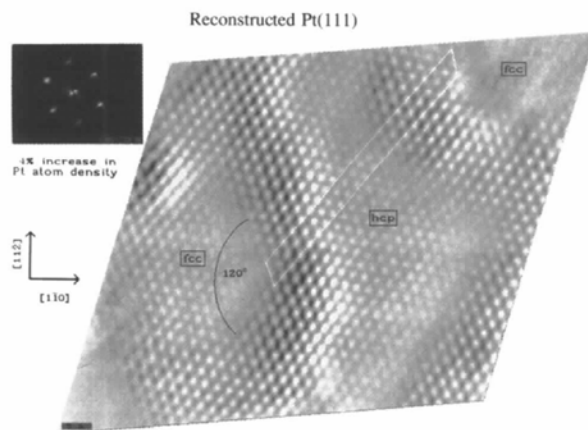


Fig. 16. Scanning tunneling microscope image of Pt(111) after carbon monoxide addition to a low-coverage sulfur overlayer. The sulfur has been pushed outside the field of view by the CO, which itself is invisible, presumably due to being constantly brushed aside by the imaging tip. The regular fine structure corresponds to atomic Pt features. The wide regions with higher brightness correspond to *fcc*- and *hcp*-terminated Pt(111), separated by darker transition bands. The inset shows a Fourier transform of the STM image, simulating a diffraction pattern which is similar to that seen for the corresponding reconstructed Au(111) surface (McIntyre, Salmeron & Somorjai, 1995).

and sulfur coadsorb on the Pt(111) face, a reconstruction is induced to a more compact, but still essentially hexagonal top-metal layer, such that parts of the surface have the outermost Pt layer located in *hcp* relationship to the underlying layers. This type of structure is stable for clean Au(111), but metastable for clean Pt(111). The mechanism for this reconstruction induced by CO and sulfur needs to be clarified. A possibility is that the CO here acts as an electron donor, since electron donors (like alkali atoms) tend to favor reconstructions of several metal surfaces. (Note that CO can also act as an electron acceptor, in different circumstances.)

4.6. Model catalysts

Many of these surface studies have direct implications for the science of heterogeneous catalysis. One can carry out reaction rate studies on single-crystal surfaces in a high-/low-pressure apparatus. The sample is cleaned under ultrahigh vacuum conditions, and then a stainless steel tube is moved over to enclose it. The tube acts as a microreactor that can be pressurized while an ultrahigh vacuum is maintained outside the stainless steel tube. Reactions can occur inside the tube as gases are circulated and the single crystal is heated. The reaction products are analyzed by gas chromatography or mass spectroscopy. After the reaction studies the gases are pumped out, the cell is opened, and the surface is re-examined in ultrahigh vacuum. Studies of this type clearly indicate that many of the surface properties which are important in understanding the structure of chemisorbed layers are also important in understanding heterogeneous catalysis.

4.7. Adsorbate-induced restructuring observed during catalysis

With a scanning tunneling microscope placed within a high-temperature/high-pressure microreactor, one can carry out a catalytic reaction and continuously monitor the surface during the reaction by scanning tunneling microscopy (STM). As shown in Fig. 8, STM readily reveals the restructuring of a platinum surface during reaction.

Similar studies indicating dynamic restructuring of surfaces were carried out by Ertl and his coworkers using photoelectron emission microscopy [PEEM (Ertl, 1994)]. The PEEM technique, although not working on the atomic scale as STM does, reveals on the micron scale the continuous restructuring of platinum and other transition metal surfaces during carbon monoxide oxidation to carbon dioxide. In this instance, various regions periodically form oxygen islands, which then react with carbon monoxide and disappear. This results in an alternation of structure that is readily noticeable and detectable as periodic changes of temperature, or spatial and time variation of the work function at the surface.

The use of structural promoters is an important part of the formulation of heterogeneous catalytic systems. In the case of iron and ammonia synthesis catalysis, alumina is added to the iron surface that produces iron aluminates. Under the reaction conditions, iron migrates onto the iron aluminate, and forms an epitaxially grown thin film with primarily (111) orientation: this is the most active surface for ammonia synthesis. This way any surface structure of iron can be restructured to form Fe(111) crystal faces. The result is that all crystal faces of iron become as active as the (111) crystal face, after suitable pretreatment of the iron catalyst.

5. Issues that need further study

Studies like those presented in this review raise a number of important general questions about the mechanisms of adsorbate-induced restructuring and about their implications for reaction steps in catalysis. Their answers are needed and would greatly benefit the fundamental understanding of catalysis. The answers would also be of great utility for understanding other chemical reaction mechanisms at surfaces, such as corrosion and even tribology (this science studies the mechanical interactions between solid surfaces, which at the atomic level also often involve bond formation and bond breaking).

One of the general questions to be clarified is: when does adsorption lead to relaxation, and when does it lead to reconstruction of the metal substrate? Systematic experimental studies are needed to identify the types of adsorbates and substrates and the coverages that give rise to the two forms of restructuring. Reconstruction is an initial phase on the path toward compound formation at the surface and then in the bulk. This issue is thus of great practical importance.

Another important issue is: to what extent can adsorption be regarded as a very localized cluster-like phenomenon? The cluster-like view, which appears successful from a structural point of view, simplifies considerably the understanding of chemical bonds and processes at surfaces. It also closely relates the surface process to the corresponding process on the smaller particles used in industrial environments.

A question of central relevance is: why do rough surfaces show better chemistry than atomically flat surfaces? As a result, it is imperative that more adsorption structures at rough surfaces be studied.

It would be most valuable to answer how exactly thermal activation breaks bonds at sequences of separate temperatures. This would clarify the sequential nature of molecular decomposition and greatly help in understanding how to guide the selectivity of catalytic reactions.

The role of coadsorption needs to be studied in more cases. Coadsorption is of course central to bringing distinct molecules to react together. In addition, it is known (for example, from vibrational measurements)

that proximity effects can be large: but they need to be elucidated and related to reactivity.

The studies performed so far point to other missing links that are needed to further elucidate the relationship between surface reactivity and restructuring abilities of surfaces and surface sites. In particular, we must carry out high-coverage studies of surface structure and bonding. High coverages are present during catalytic reactions. Such studies would permit us to learn about the structural surface arrangements that occur during catalysis at high pressures.

We must also carry out time-resolved investigations of short-lived adsorbates. Most of the adsorbates studied to date are stagnant on surfaces and do not turn over during the catalytic reaction because of their strong chemisorption bonds. Reactions occur in the presence of these stagnant overlayers. It is very important that by using time-resolved methods we focus on short-lived species that are removed from the surface within times shorter than or equal to turnover times. By time resolution we should be able to distinguish between stagnant molecules and reactive intermediates.

Finally, time-resolved studies of the dynamics of adsorbate-induced restructuring should be carried out. The surface chemical bond is always between the adsorbate and the substrate. Therefore, it is imperative that we use techniques that can simultaneously monitor the structure and structural changes on both sides of the chemical bond: on the adsorbate side and the substrate side.

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