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ADSORBATE-INDUCED RESTRUCTURING OF SURFACES

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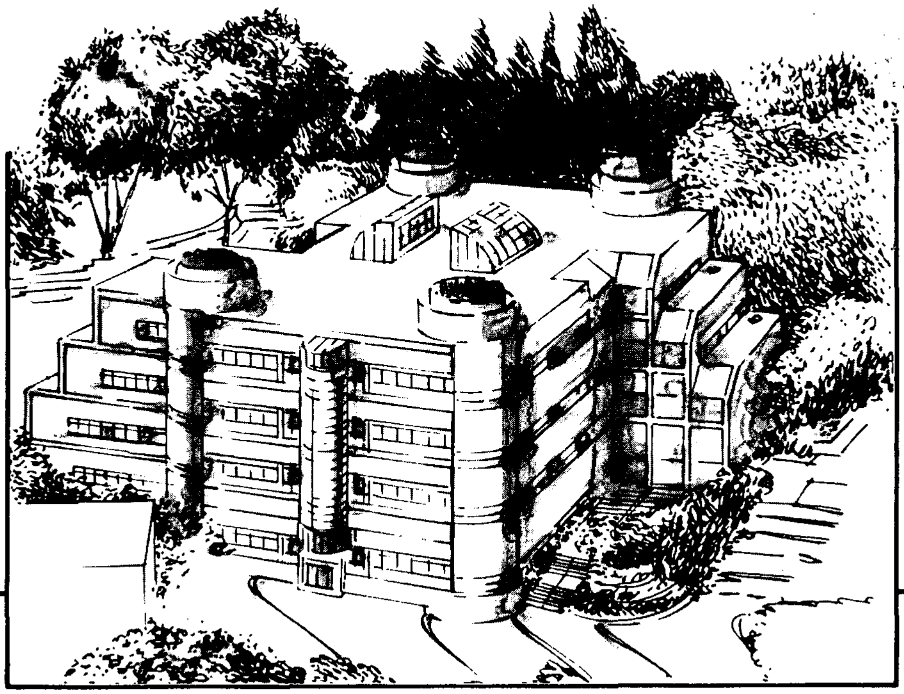

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Abstract

Adsorbed atoms and molecules frequently cause restructuring of single-crystal surfaces, ranging from small atomic relaxations and reconstructions to macroscopic shape modifications. The occurrence of such adsorbate-induced restructuring is reviewed, and the mechanisms and dynamic time scales are discussed. The importance of adsorbate-induced restructuring in a variety of surface processes is stressed. It is proposed that such restructuring can explain the observed "structure insensitivity" of a class of catalytic reactions, and that it could play a major role in most forms of reactivity.

Contents

1. Introduction

In the early nineteen fifties a physical model of a surface would typically be a flat plane, representing the termination of the condensed phase and devoid of atomic structure. Such a model could explain the properties of the surface space charge[1] and the variation of the work function from one crystal face to another.[2] It was also satisfactory for the development of surface thermodynamic parameters to explain Gibbs surface segregation,[3] the Langmuir adsorption isotherm[4] and surface tension.[5]

Then, studies of surface structure and chemisorption using single-crystal surfaces and small metal tips revealed the constant presence and the large concentration of atomic steps, usually one atom in height, separated by terraces which are atomically well ordered.[6] The ordering of these steps on higher-Miller-index crystal faces gives rise to electron diffraction features that facilitated studies of their structure.[7] Figure 1 shows a recent scanning tunneling microscope image of the (0001) surface of rhenium,[8] that looks flat by electron diffraction although it is in fact full of steps. Kink sites, where steps show atomic irregularities, were also frequently observed via electron diffraction.[7]

The omnipresence of steps and of kink sites gave strong endorsement to terrace-step-kink models of crystal growth and evaporation developed in the early days of surface science:[9,10] these sites were invoked to play dominant roles in controlling the kinetics of these phase changes, which occur at the surface. Surface irregularities, steps and kinks were also found to play major roles in surface chemical reactions and were found to be partly responsible for the surface structure sensitivity of many catalytic processes.[11]

Both the flat and step models of surfaces assumed a rigid lattice in which the surface atoms retained their clean-state equilibrium positions during adsorption or during surface reactions. However, it has recently become abundantly clear that the presence of extra atoms on a surface can restructure that surface. New surface science studies reveal that, during surface chemical processes, marked changes frequently occur in the locations of surface atoms in the substrate. The act of adsorption gives rise to a dynamic change of surface structure, often reversible, sometimes permanent. Thus, *the surface structure cannot be viewed as being static during adsorption or during catalytic reactions but changes markedly as the nature and concentration of adsorbates are varied.*

In this paper we focus on and review this surface phenomenon, *adsorbate-induced restructuring*, which appears to be all-pervasive. Adsorbates are foreign atoms of a different chemical element than the substrate material. Adsorbates may be individual atoms or molecules or any other cluster of atoms. The stronger the adsorbate-substrate bond, the more likely that restructuring of the surface occurs. Thus, physisorption, with its

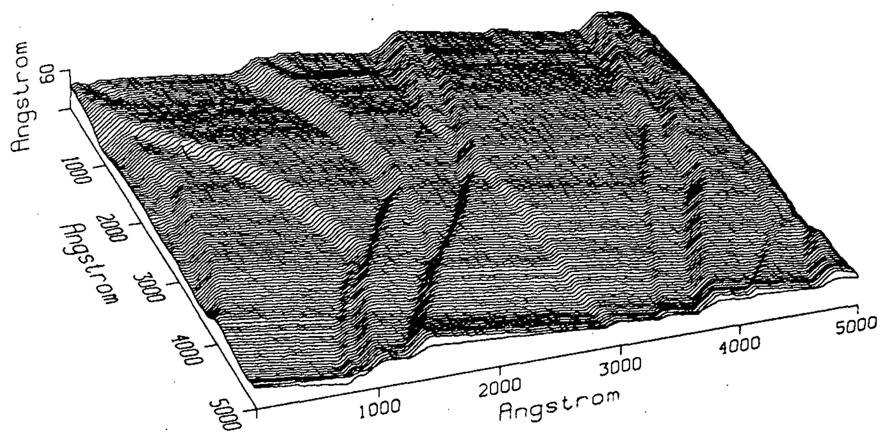

Fig. 1. Scanning Tunneling Microscope image of a Re(0001) single-crystal surface, saturated with sulfur and taken in air. Ledges correspond to atomic steps of varying height (see scale at upper left; a single-atom step is about 2 Å high). They separate flat terraces of (0001) crystallographic orientation.

weak bonding to the substrate is not known to cause any detectable restructuring. Chemisorption does frequently imply restructuring, whether the adsorbate-substrate bond is covalent or ionic, and whether or not the bonding is accompanied by charge transfer.

There are different kinds of adsorbate-induced restructuring, ranging from mild local relaxations via moderate local reconstructions to drastic macroscopic reshaping. We shall review their occurrence and discuss their mechanisms and dynamic time scales. We shall also consider the role of adsorbate-induced restructuring in important surface processes, including the formation of active sites in catalysis and the phenomenon of cyclic reconstructions. We also propose that such restructuring is one explanation for the "structure-insensitivity" of a class of catalytic reactions, and that it often may be responsible for the bond breaking of adsorbates, i.e. be the cause of reactivity.

Tabulations of surface structure results, including many to be discussed here, are available in the literature.[12-16] Below, we shall provide tables of surface structures formed by adsorbate-induced restructuring, classified according to type of restructuring.

2. The Nature of Clean Surfaces

Before describing the phenomenon of adsorbate-induced restructuring, we shall summarize the main structural properties of clean surfaces. We shall call a surface ideal when it is obtained by a truncation of the three-dimensional bulk crystal lattice, such that all atomic nuclei are frozen in their bulk lattice sites. Many close-packed clean metal surfaces fall in this category, within the uncertainty of the experimental techniques of surface crystallography, which is on the order of 0.01 to 0.03Å. Examples are the (111) and (100) faces of many face-centered cubic (fcc) metals, such as Ni, Cu, Rh, Pd and Ag.

Often, small variations in bond lengths and bond angles of atoms in the surface occur to accommodate the changed environment of the interface to produce a relaxed surface. Measurable relaxations (i.e. atomic displacements of about 0.03Å or more) are found at less close-packed clean metal surfaces, such as the (110) face of most fcc metals, including Ni, Cu, Rh, Pd and Ag. Typical is a contraction of the spacing between the first and second atomic layers perpendicular to the surface plane (z direction), followed by an expansion between the next two layers. Such relaxations can be found even deeper in the surface, but they decay exponentially in magnitude with depth.

Lateral displacements, parallel to the surface (x-y directions), also occur at clean unreconstructed surfaces. The main example is that of step edges, due to their asymmetry parallel to the surface: an atom at a step edge will tend to be pulled not only in the z direction into the surface but also laterally towards the upper terrace, i.e. in the direction where most of its bonding partners are located.

Several clean semiconductor surfaces are also relaxed, such as the (110) face of GaAs and other III-V compounds. Here the relaxations usually occur in directions both perpendicular and parallel to the surface and can have relatively large amplitudes (up to about 1Å). They often consist of substantial bond rotations, in addition to bond length changes.

The presence of a surface may also cause local bond breaking and new bond formation, which we shall call reconstruction. In this case, the bulk bonding arrangement is no longer the preferred one and a new bonding configuration takes over at the surface. This occurs primarily with solid surfaces in which there is a preference for directional bonding and an energetic disadvantage due to unsatisfied "dangling" bonds; semiconductor surfaces are prominent examples. A totally new surface lattice may be created, which may be unknown in the bulk. Examples are the reconstructions of the (100) and (111) faces of Si and Ge.

Several metal surfaces also reconstruct. The causes here are more subtle, including bond length reduction and electronic relaxations. Often thermally-induced phase transitions to other surface structures are possible due to smaller total-energy differences between structures. Examples of reconstructed clean metal surfaces are: Mo(100) and W(100), Ir(100) and (110), Pt(100) and (110), and Au(111), (100) and (110).

Larger-scale restructuring of clean surfaces is also possible, with the help of diffusion of atoms along the surface over distances much larger than atomic diameters. This permits a macroscopic reshaping of the surface, such as in facetting. It has recently become evident that clean surfaces can undergo such restructuring in suitable temperature ranges. Thermally-induced roughness has been seen for the stepped surfaces Cu(113), (115) and Cu(1,1,11), as well as Ni(113), as detected by atom diffraction. Above a roughening transition temperature, the steps lose their linearity and become increasingly curved.[17,18] As a result, the surface itself becomes less planar and roughening takes place perpendicular to the original surface. Facetting has been observed with vicinal (stepped) Si(111) surfaces at temperatures below the (7x7)-to-disorder transition. In this case, steps bunch together, yielding larger terraces of reconstructed Si(111), separated by groups of many closely packed steps.[19]

3. Surface Relaxations Due to Adsorption

When atoms or molecules adsorb on relaxed clean surfaces and form chemical bonds, the surface atoms are placed in a different chemical environment. They change their equilibrium positions as a result. Upon adsorption, any clean-surface relaxation is generally reduced, as the surface atoms of the substrate move back towards the ideal bulk-like positions. This phenomenon is perhaps the simplest form of adsorbate-induced restructuring of surfaces.

Good examples of the relaxation of interlayer spacings (in the z direction) are provided by atomic adsorption on the (110) surfaces of Ni and other fcc metals. The clean fcc(110) surfaces typically exhibit contractions by about 10% (0.1 to 0.15Å) in the topmost interlayer spacing relative to the bulk value. Upon adsorption, these contractions are reduced to less than 3 to 4% (0.03 to 0.05Å), often indistinguishable from the bulk value.

Table 1 lists further examples supporting the general principle of reduction of relaxations perpendicular to the surface due to adsorbates.

In addition, adsorbates can induce new relaxations of a type that does not occur in the clean surface. Often these are atomic displacements parallel to the surface, rather than perpendicular to the surface. Typically, an adsorbed atom will induce lateral displacements that provide better bonding to the substrate.

This is well illustrated by S on Fe(110), as shown in Fig. 2. The clean Fe(110) surface provides two-fold and three-fold coordinated adsorption sites of high symmetry. Apparently, sulfur maximizes its coordination number to nearly four by distorting the two-fold coordinated site into a nearly square "hollow" site.

Other examples are provided by carbon as well as nitrogen on Ni(100), Fig. 3. The adatom manages to penetrate the Ni(100) surface so as to bond not only to four first-layer Ni atoms but also to a Ni atom in the second metal layer. This is achieved by expanding a four-fold hollow site around the adatom. The surrounding metal lattice does not accept a corresponding compression (because nearby adatoms also cause expansions), and instead forces a rotation of the square of four Ni atoms about the surface normal. Thereby the average metal density in the top layer is kept constant.

A semiconductor example is shown in Fig. 4: Sb adsorbed on GaAs(110) removes the relatively large up, down and lateral displacements of the Ga and As atoms in the topmost layer of the clean surface. Other cases of adsorbate-induced relaxations with components parallel to the surface are given in Table 2.

Table 1. Adsorbate-induced reductions of clean-surface spacing relaxations. Shown are the expansions of the topmost (and second, when available) metal-metal interlayer spacings, from the clean surface relaxations, in percent of the bulk spacing value. Thus, "10% from –5%" would imply that the clean surface has a –5% contraction relative to the unrelaxed bulk spacing, and the adsorbate-covered surface has an expansion of –5+10 = +5% relative to the unrelaxed bulk spacing.

Surface	Description	Reference
Fe(100)-c(2x2)-N	11.5% from -1.4%	20.
Fe(100)-(1x1)-O	9% from -1.4%	21.
Fe(100)-c(2x2)-S	3% from -5%	22.
Co(100)-c(2x2)-O	4% from -4%	23.
Ni(110)-(2x1)-2H	4% (1.5%) from -8.5% (3.5%)	24.
Ni(100)-c(2x2)-O	8% from -5%	25.
Ni(110)-c(2x2)-S	19% (-7%) from -8.5% (3.5%), with buckling by 11% of the second Ni layer	26.
Ni(100)-c(2x2)-S	4% from 0%, with some bucking of the second Ni layer	27.
Cu(110)-"(1x1)"-H	9% (0%) from -8% (2.5%)	28.
Cu(100)-c(2x2)-Cl	2.5% from 0%	29.
Cu(100)-c(2x2)-N	8% from 0%	30.
Mo(100)-c(2x2)-N	9.5% from -9.5%	31.
Mo(100)-c(2x2)-S	7% from -9.5%	32.
Mo(100)-(1x1)-Si	9.5% from -9.5%	33.
Rh(110)-(1x1)-2H	5% from -7%	34,35.
Rh(110)-c(2x2)-S	3% from -3%	36.
Pd(110)-(2x1)-2H	4% (2%) from -6% (1%)	35.
Pd(111)-$(\sqrt{3}\times\sqrt{3})R30°$-CO	5% from 1%	37.
Ag(110)-(2x1)-O	7% from -7%	38.
W(100)-(1x1)-2H	4% from -6%	39.
Ir(110)-(2x2)-2S	9% (10%) from -12% (-12%) (both the clean and the S-covered surface have the missing-row reconstruction)	40.

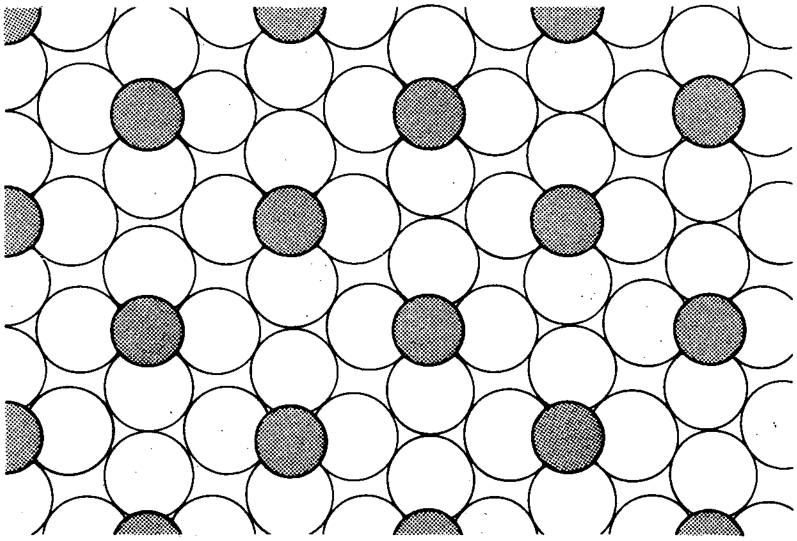

Fig. 2. Structure of Fe(110)-(2x2)-2S, with S shown as gray circles, in top view.

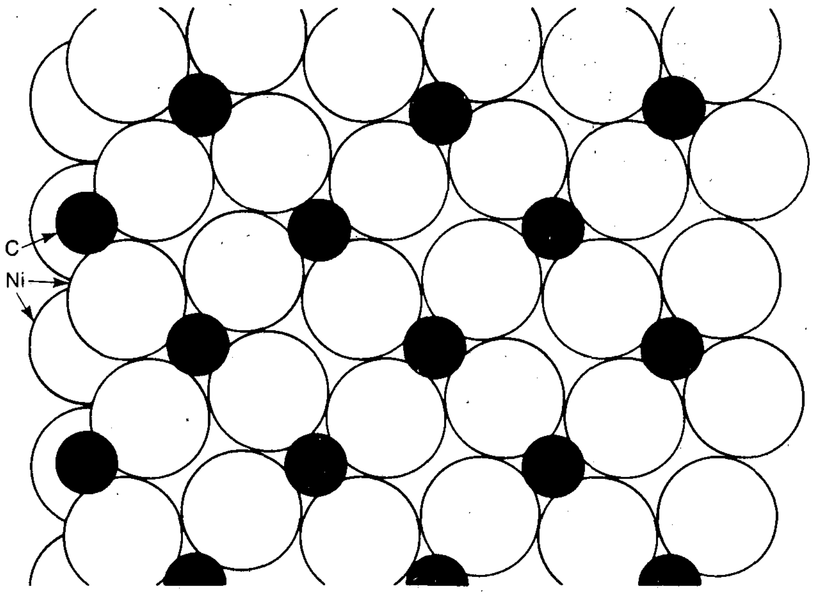

Fig. 3. Structure of Ni(100)-(2x2)-2C, with C shown as filled circles, in top view.

4. Local Reconstructions Induced by Adsorption

Table 3 gathers examples where the substrate undergoes bond breaking and rebonding as a result of adsorption. Several categories may be distinguished.

A. Removal of reconstruction by adsorption

Adsorbates frequently destroy existing reconstructions of clean surfaces. The substrate then usually takes on the bulk structure again. It appears that the adsorbate substitutes for the missing atoms due to the original creation of the surface: the adsorbate places the surface atoms in a more bulk-like environment. However, even small amounts of adsorbate, as little as 10% of a monolayer, may be sufficient to destroy a reconstruction. Removal of the adsorbate (such as by thermal desorption) reverses the process: the clean-surface reconstruction reappears again. But kinetic effects may trap a metastable state of the surface, as has been observed with small amounts of adsorbates on Ir and Pt(100).[52,90,104,105]

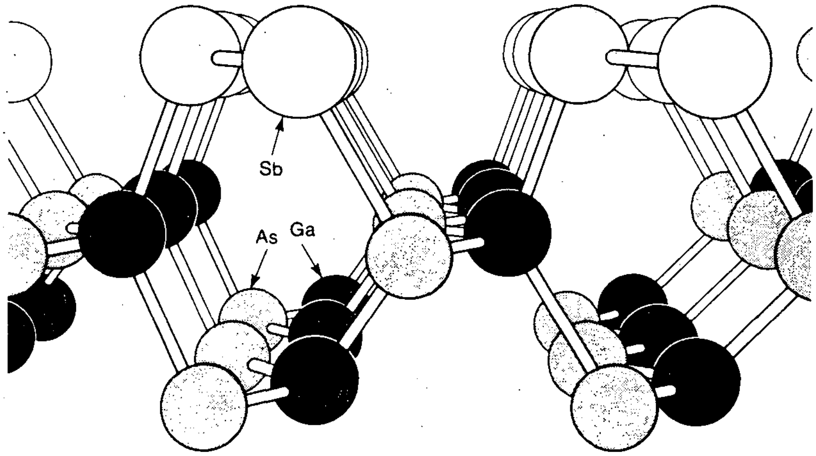

Fig. 4. Structure of GaAs(110)-(1x1)-Sb, in side view, with the surface at the top.

Table 2. Adsorbate-induced relaxations parallel to the surface.

Surface	Description	Reference
Fe(110)-(2x2)-2S	squaring of hollow site	41.
Ni(100)-(2x2)-2C	rotation of hollow site	42.
Ni(100)-(2x2)-2N	rotation of hollow site	43.
Cu(100)-(2x2)-S	lateral (as well as perpendicular) displacements in the two topmost Cu layers	44.
Mo(100)+H	incommensurate pattern of lateral Mo displacements	45.
Rh(110)-(1x2)-H	shift and buckling in first Rh layer	46.
Rh(100)-(2x2)-O	weak Rh reconstruction with p2gg symmetry	47.
W(100)+H	commensurate and incommensurate patterns of lateral W displacements	48.
W(100)+N	surface compound formation	49.
W(100)+O	removal of clean-surface reconstruction and shrinking of hollow site	50.

Removal of the hexagonal top-layer reconstruction of the (100) faces of Ir, Pt and Au has been seen following the adsorption of, for example, CO molecules.[90,91] Many examples exist for semiconductor surfaces: for instance, hydrogen removes the reconstructions of clean Si(111)[52] and diamond C(111),[51] the latter illustrated in Fig. 5, by restoring a bulk termination and saturating the "dangling bonds".

However, if one uses an electron donor as an adsorbate on a metal, such as alkali atoms, the clean-surface reconstruction may not disappear. Electron-donating adsorbates tend to stabilize or even induce metal reconstructions. Stabilization is exemplified by alkali adsorption on the hexagonal reconstructions of Ir(100).[87] There the clean-surface reconstruction is maintained in the presence of alkali atoms.

B. Creation of reconstruction by adsorption

An unreconstructed clean substrate can be induced to reconstruct by adsorbates. This occurs in particular with alkali atoms adsorbed on Ni,[74] Cu,[75] Pd[82] and Ag(110).[83] Even with a small fraction of a monolayer of alkali metals, these metal surfaces take on the "missing-row structure", in which every other row of close-packed surface atoms is missing. A likely reason for this is that large alkali atoms bond more strongly within the deep troughs due to the missing rows than in the shallow troughs of the ideal (110) surface.[74,106]

C. Change of reconstruction by adsorption

There are cases where a clean-surface reconstruction is changed by an adsorbate into another type of reconstruction. Hydrogen on W(100) and Mo(100) provides examples of this process.[48,45] Clean W(100) and Mo(100) are characterized by a reconstructed surface with long zigzag chains of surface metal atoms. When hydrogen is adsorbed, the tendency is to break up these chains into individual W-H-W or Mo-H-Mo trimers. Each H atom bridges a pair of W or Mo atoms, replacing the zigzag chain geometry.

The adsorption of metals on semiconductors also induces different reconstructions. However, little is known so far about the details of most of these structures. But it seems clear that these cases appear to signal the occurrence of a more pervasive type of reconstruction, compound formation, to be discussed next.

D. Compound formation induced by adsorption

In compound formation, a reconstruction occurs that involves a stoichiometric mix of the substrate and adsorbate atoms. Continued addition of adsorbate atoms may enable the formation of a thicker compound film. Such behavior is characteristic of oxidation, nitridation, carbide formation and alloying of metal surfaces. Figures 6, 7 and 8 give examples of oxidation of metal surfaces. Ta(100) is shown after uptake of a submono-

Table 3. Local reconstructions induced by adsorbates. The nature of the resulting structure is described.

Surface	Description	Reference
C(111)-(1x1)-H	removal of clean-surface reconstruction of diamond(111)	51.
Si(100)+H	removal of clean-surface reconstruction	52.
Si(111)+N	removal of clean-surface reconstruction	53.
Si(111)+O	removal of clean-surface reconstruction	54.
Si(111)+Al	removal of clean-surface reconstruction	55.
Si(111)+Ti	removal of clean-surface reconstruction	56.
Si(111)+Co	removal of clean-surface reconstruction	57.
Si(111)+Ni	removal of clean-surface reconstruction	58.
Si(111)+Cu	removal of clean-surface reconstruction	59.
Si(111)+Ga	removal of clean-surface reconstruction	60.
Si(111)+As	removal of clean-surface reconstruction	61.
Si(111)+Se	removal of clean-surface reconstruction	62.
Si(111)+Br	removal of clean-surface reconstruction	63.
Si(111)+Ag	removal of clean-surface reconstruction	64.
Si(111)+In	removal of clean-surface reconstruction	65.
Si(111)+Sn	removal of clean-surface reconstruction	66.
Si(111)+Pt	removal of clean-surface reconstruction	67.
Si(111)+Au	removal of clean-surface reconstruction	68.
Si(111)+Pb	removal of clean-surface reconstruction	69.
Si(111)+Bi	removal of clean-surface reconstruction	70.
Fe(211)-(2x1)-O	missing rows	71.
Ni(110)-(1x2)-2H	row pairing	72.
Ni(110)-(1x2)-O	substitution for missing rows	73.
Ni(110)+K	missing rows	74.
Cu(110)+Li	missing rows	75.
Cu(110)-(1x2)-O	missing rows	76.
Ge(111)-(1x1)-H	removal of clean-surface reconstruction	77.
Ge(111)+Br	removal of clean-surface reconstruction	78.
Ge(111)+Sn	removal of clean-surface reconstruction	79.
Ge(111)+Pb	removal of clean-surface reconstruction	80.
Pd(110)-(1x2)-H	missing rows	81.
Pd(110)-(1x2)-Na or Cs	missing-row reconstruction	82.
Ag(110)-(1x2)-Li or K or Cs	missing-row reconstruction	83.
W(100)+H	removal of clean-surface reconstruction and creation of new coverage-dependent reconstructions	48.
W(100)-(5x1)-C	removal of clean-surface reconstruction and creation of new reconstruction	84.
Ir(110)+O	removal of clean-surface reconstruction	85.
Ir(100)+various adsorbates, esp. alkali	removal of clean-surface reconstruction	86, 87.
Pt(100)+O	removal of clean-surface reconstruction, then surface compound formation	88.
Pt(100)-c(4x2)-Cs	removal of clean-surface reconstruction	89.
Pt(100)+CO	removal of clean-surface reconstruction	52, 90, 91.
Pt(110)+many adsorbates	removal of clean-surface reconstruction	92, 93, 94, 95.
Au(110)+metals	removal of clean-surface reconstruction	96, 97, 74.
Au(100)+S and many metal adsorbates	removal of clean-surface reconstruction	98, 99.
Au(111)+mainly metal adsorbates	removal of clean-surface reconstruction	99.
Ge(111)-(2x2)-S	removal of clean-surface reconstruction	100.
Ge(111)-(1x1)-Cl	removal of clean-surface reconstruction	101.
Si(111)-(1x1)-Cl	removal of clean-surface reconstruction	101.
GaP(110)-(1x1)-Al	GaAl(110) formation	102.
GaAs(110)-(1x1)-Sb	change of clean-surface parallel and perpendicular distortions	103.

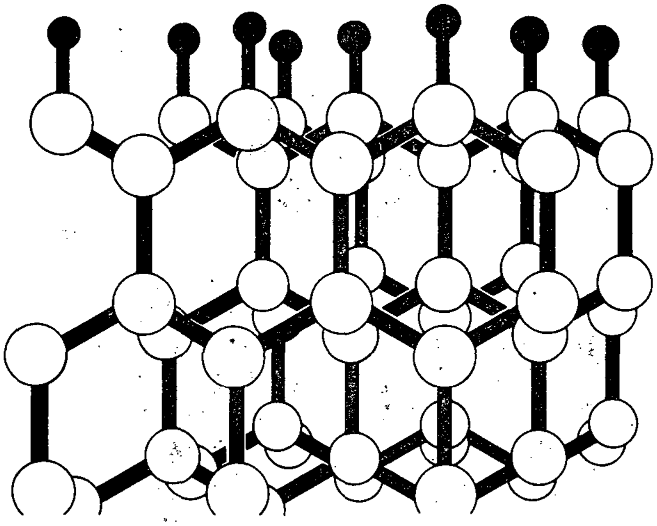

Fig. 5. Structure of diamond C(111)-(1x1)-H, in side view, with H (dark circles) occupying each dangling bond.

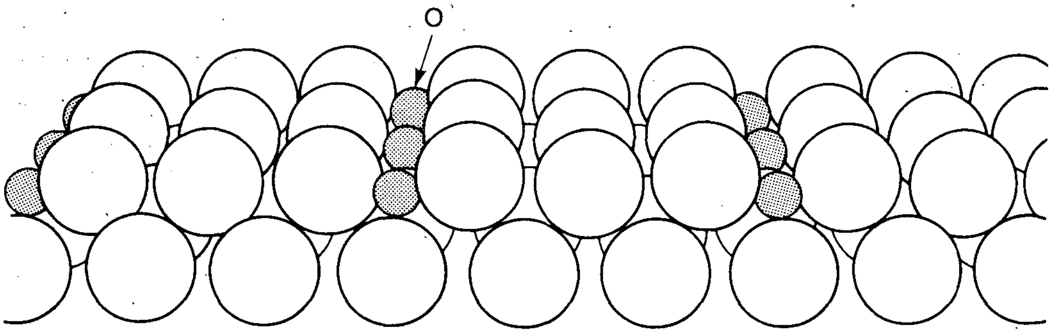

Fig. 6. Structure of Ta(100)-(1x3)-O, in side view.

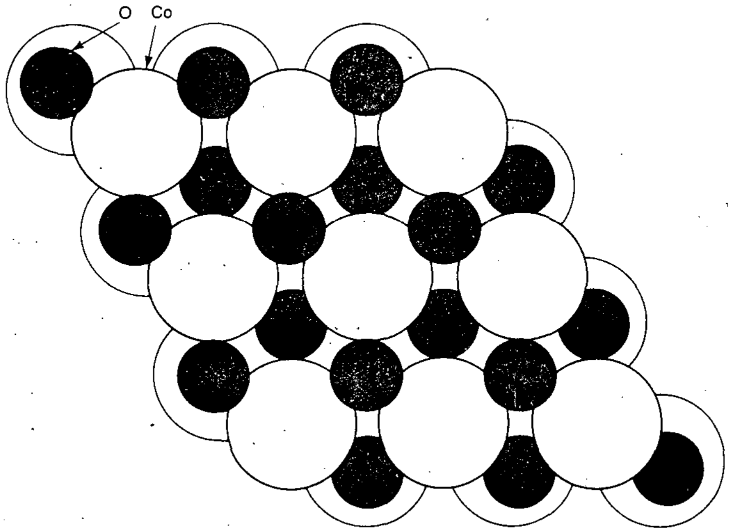

Fig. 7. Structure of CoO(111) grown on Co(111) (invisible), in top view.

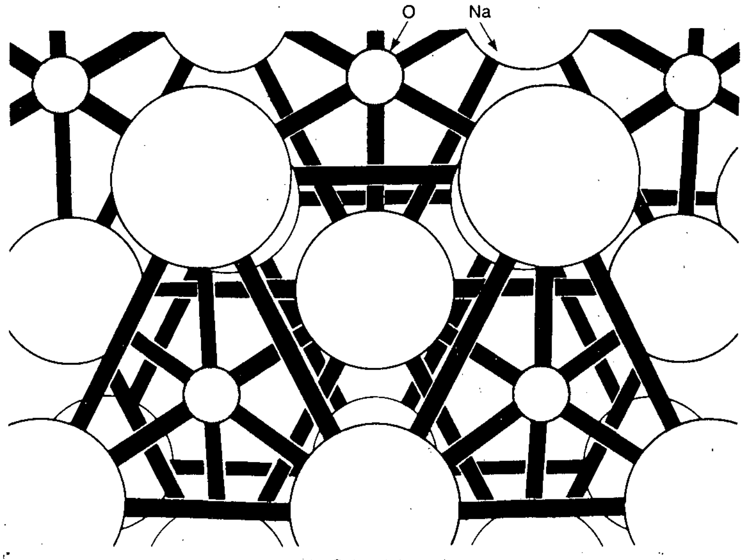

Fig. 8. Structure of $Na_2O(111)$ grown on Na(110) (invisible), in top view.

layer amount of oxygen, which takes interstitial positions between the first and second metal layers. Oxides formed on Co(111) and Na(110) are shown, which have grown to a thickness larger than the electron mean free path of surface science techniques. Here one obtains a near-perfect termibation of a bulk oxide lattice. Figure 9 illustrates an intermediate nitridation step, consisting of the penetration of one monolayer's worth of N atoms between the first and second metal layers.

Compound formation is also common in the formation of metal silicides after adsorption of metal atoms onto silicon surfaces. Thus, upon Ni deposition on Si(111), $NiSi_2$ grows with its (111) surface interfaced to the substrate, as shown in Figure 10. Cobalt and other transition metals behave similarly. Figure 11 illustrates the case of Al forming a substitutional GaAsAl compound after deposition on GaAs(110). Table 4 provides many more examples.

The thickness of the resulting compound may be limited by the kinetics of these solid-state reactions. The diffusion of the adsorbate through the compound film may be very slow and, in some instances, effectively stop the compound formation. The formation of a 30Å thick aluminum oxide film by oxidation of aluminum surfaces is a well-known example.

E. Adsorbate induced surface segregation

Adsorbates may induce large changes of surface composition in multicomponent systems. Such changes involve atomic diffusion perpendicular to the surface, and thus bond breaking and rebonding. This occurs particularly when the chemisorption bond energies between the alloy components are very different (Table 5).

One example is the behavior of the Ag-Pd alloy.[168] The clean surface of a Ag-Pd alloy is enriched in silver at any bulk composition because of the lower surface energy of Ag as compared to Pd. Upon adsorption of CO, the surface composition changes rapidly. Because of the greater strength of the Pd-CO bond as compared to the Ag-CO bond, the Pd atoms move to the surface and the alloy surface becomes enriched in Pd. Upon heating CO desorbs and the surface excess of Ag is reestablished.

Mn surface segregation has been observed upon oxygen adsorption on Cu-Mn and Ag-Mn films. Multilayer enrichment of Mn is observed.[169] An example at a semiconductor surface is the surface enrichment in indium due to Co adsorption on the InP(110) surface.[170]

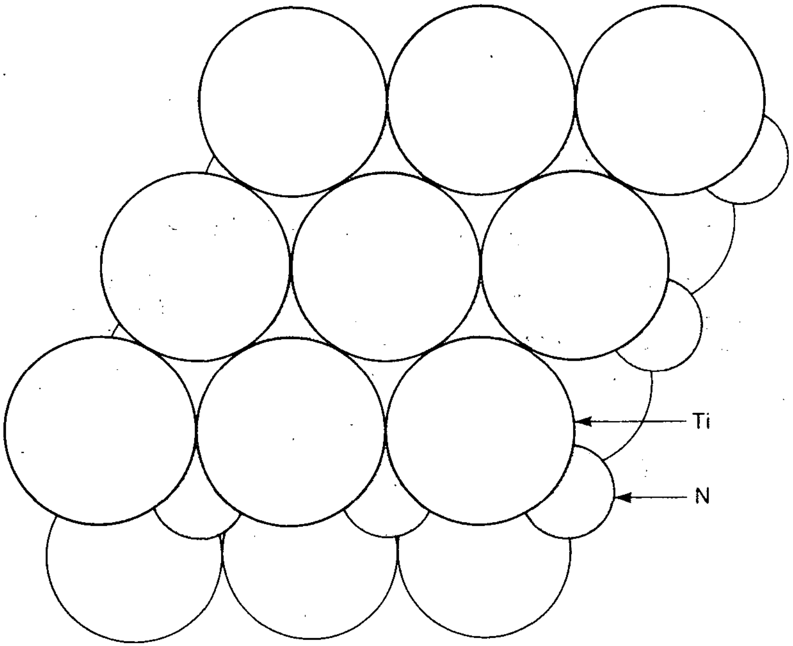

Fig. 9. Structure of Ti(0001)-(1x1)-N, in top view, with N occupying interstitial sites between the first and second metal layers.

5. Macroscopic Reshaping Induced by Adsorption

Adsorbates can change the shape of a surface on a scale much larger than atomic dimensions. Atomic diffusion, especially parallel to the surface, is a crucial component of such restructuring. Facetting and compound crystallite formation are perhaps the most common examples of such restructuring. Long time scales (often on the order of hours) are characteristic of this class of restructuring.

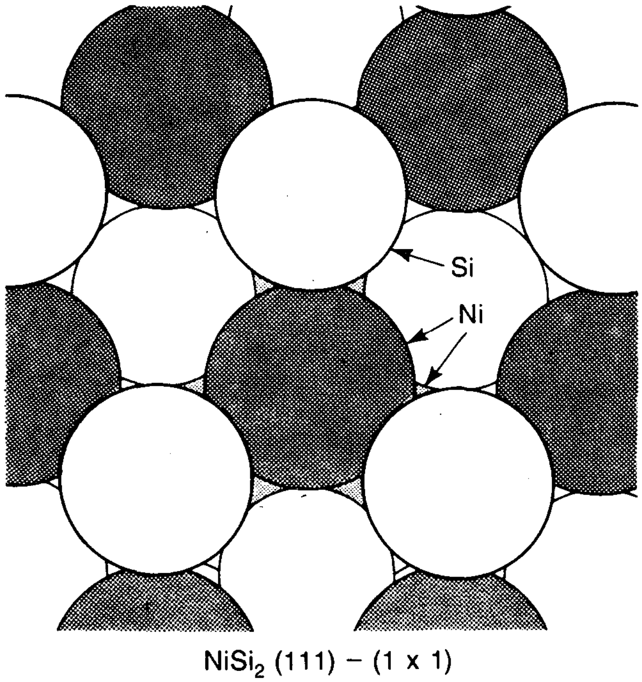

Fig. 10. Structure of $NiSi_2(111)$ grown on Si(111) (invisible), in top view.

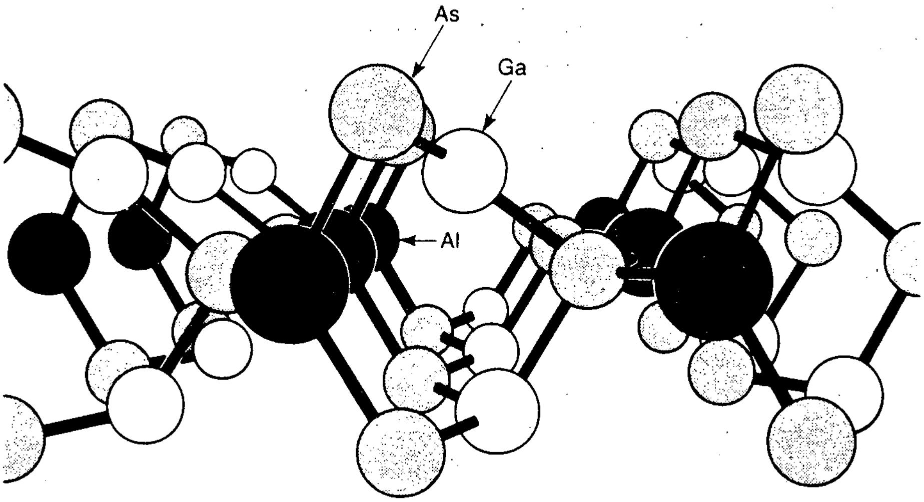

Fig. 11. Structure of GaAs(110)-(1x1)-Al, in side view, with Al substituted for second-layer Ga atoms.

Table 4. Compound formation.

Surface	Description	Reference
oxides		
Be(0001)+O	BeO(0001) formation	107.
Na(0001)+O	Na_2O(111) formation	108.
Mg(0001)+O	MgO(111) formation	109.
Al(111)-(1x1)-O	O underlayer in AlO arrangement	110.
Al(111)+O	oxide formation	111.
Cr(110)+O	Cr_2O_3 formation	112, 113.
Cr(100)+O	Cr_2O_3(310) formation	112.
Fe(100)+O	FeO(100), (111) and (110) formation	114, 115.
Fe(110)+O	FeO(111) formation	116.
Co(111)+O	CoO(111) surface compound formation	117.
Ni(100)+O	NiO(100) and (111) formation	118, 119.
Ni(111)+O	NiO(111) formation	120.
Ni(211)+O	NiO formation	121.
Zn(0001)+O	ZnO(0001) formation	122.
ZnSe(110)+O2	ZnO(0001) formation	123.
Sr(100)+O	SrO(100) formation	124.
Zr(0001)-(2x2)-O	O interstitials as underlayer	125.
Nb(100)+O	NbO_2 formation	126.
Nb(110)+O	NbO formation	127.
Mo(111)+O	MoO_2(100) formation	128.
Mo(100)+O	MoO_2(110) formation	129.
Rh(111)+O	Rh_2O_3(0001) formation	130.
Pd(100)+O	oxide formation	131, 132.
Ta(100)-(1x3)-O	O interstitials as underlayer	133.
W(110)+O	WO_3(111) formation	134.
Re(S)-[6(0001)x(16-76)]+O	ReO_3 formation	135.
Ir(111) or (110)+O	oxide formation	136, 137.
Pt(111) or (100)+O	PtO_2(0001) formation	138, 88.
Pt(110)+O	PtO formation	92.
Au(S)-[6(111)x(100)]+O	oxide formation	139.
Pb(100)+O	PbO(100) formation	140.
Bi(0001)+O	BiO formation	141.
Th(111)+O or CO	ThO_2(111) formation	142.
Th(100)+O	ThO_2 formation	143.

Table 4. Compound formation (continued).

Surface	Description	Reference
nitrides		
Ti(0001)-(1x1)-N	N interstitials as underlayer	144.
Fe(12,1,0)+N	nitride formation	145.
Cu(100)-c(2x2)-N	surface compound formation	30.
W(100)+N	surface compound formation	49.
carbides		
Co(10-12)+CO	Co_3C(001) formation	146.
Ni(100)+C	carbide formation	42.
Hf(100)+C	carbide formation	147.
Ta(100)+C	carbide formation	148.
W(100)+(5x1)C	carbide monolayer formation	84.
other compounds		
C(0001)+K	intercalate of K in graphite	149.
Cr(100)+Br	$CrBr_2$ formation	150.
Si(111)+Co	$CoSi_2$ formation	151.
Si(111)+Ni	$NiSi_2$(111) formation	152.
Si(100)+Ni	$NiSi_2$(100) formation	153.
Si(111) or (100)+Pd	Pd_2Si formation	154.
Ni(100)+S	Ni_3S_2 formation	155.
Ni(100)+I	NiI_2 formation	156.
Cu(100)+Pd	alloy formation	157, 158.
Pd(111)+Cl	$PdCl_2(1\bar{1}0)$ formation	159.
GaAs(110)+Al	GaAlAs(110) formation by substitution of Al for Ga	160.
Mo(100)+S	MoS_2(100) formation	161.
Ag(111)+Cl	AgCl(111) formation	162.
Ag(111)+S	Ag_2S(111) formation	163.
Pt(111)+Cu	alloy formation	164.
Au(111)+Si	AuSi formation	165.
Bi(0001)+Cl	$BiCl_3$ formation	166.

A. Restructuring of stepped surfaces by adsorption

After proper preparation, stepped surfaces often exhibit ordered steps of mono-atomic height separated by flat terraces. With some surfaces, such as those of semiconductors, two-atom-high steps are most frequent. Adsorbates have frequently been observed to restructure such surfaces, as Table 6 illustrates. Often preferential adsorption at step sites multiplies the step height. Desorption of the adsorbate reestablishes the clean-surface step heights.

Table 5. Change in composition.

Surface	Description	Reference
MoO_3(010)+O	MoO_2 formation	167.
AgPd alloy + CO	surface enrichment in Pd	168.
Cu-Mn or Ag-Mn films + O	surface enrichment in Mn	169.
InP(110)+Co	surface enrichment in In	170.

Table 6. Facetting and step modification.

Surface	Description	Reference
Al(110)+O	(331) and (111) facetting	171, 172.
Si(100)+NH_3	(111) facetting	173.
Si(100)+Pd	(111) facetting	174.
Si(111) stepped + Ni or Pd	(221) facets	175.
Si(211)+H	facetting	176.
Si(hkl) [(001) zone]+Au	facetting	177.
Ni(210)+N	(100) and (110) terrace formation	178.
Cr(110)+O (100)	facetting	112.
Ni(210) to (410)+O	facetting	179.
Ni(hk0)+O	to (100), (410) and (210) facets	179.
Cu(hk0)+O	to (320), (750), (530) and (110) facets	180.
Cu(100)+O	(410) facetting	181.
Cu(210)+O	(410) and (530) facetting	181.
Cu(211)+O	5(111)x2(100) facetting with double-height steps	182.
Cu(841)+O	(410) and (100) facetting	183.
Nb(750)+O	(110) terrace and (310) step formation	184.
Mo(100)+O	(110) and (112) facetting	129.
Rh(331)+O	facetting	185.
Rh(S)-[6(111)x(100)]+O	12(111)x2(100) facetting with double-height steps	185.
Ta(211)+N	(311) facetting	186.
W(111)+Cl	facetting	187.
W(111)+O or CO	(211) facetting	188.
W(100)+O	(110) facetting	189.
Pt(997)+O	17(111)x2(11-1) facetting with double-height steps	190.
Pt(S)-[4(111)x(100)]+H	facetting	191.
Pt(S)-[5(100)x(111)] or [6(111)x(100)] or [13(111)x(310)]+O	terrace broadening	192.
Pt(S)-[6(111)x(100)]+H	11(111)x2(100) facetting with double-height steps	193.

B. Adsorbate induced compound crystallite formation

Associated with compound formation, one may observe a macroscopic change in the shape of the surface. For instance, differently oriented facets of microcrystallites can form due to the particular way in which the compound lattice is attached to the substrate lattice. An example of such facet formation was observed with the oxidation of Mo(100).[129]

C. Adsorbate induced recrystallization

Adsorbates bind more strongly to one crystal face than another and can thus force a recrystallization of the substrate to expose a more favorable face that offers stronger-binding sites. For instance, 4-fold coordinated sites might bind a particular adsorbate more strongly than 3-fold sites. In order to minimize the surface free energy, the surface would then restructure to expose more 4-fold than 3-fold sites. Thus, face centered cubic particles with (111) surface orientations would restructure to expose faces with (100) orientations.

The sulfur adsorption induced reconstruction of the Ni(111) crystal face to Ni(100) is one example of this effect.[194] Other examples include the adsorption of oxygen on iron, tungsten or nickel, all of which cause massive reorganization of the metal surfaces.

Another example of recrystallization is the alumina-induced restructuring of iron. Alumina is a so-called structural promoter of iron catalysts used in the synthesis of ammonia. This is a structure sensitive catalytic reaction that occurs at a rate that is more than two orders of magnitude faster over the Fe(111) and (211) crystal faces than over the close packed Fe(110) face.[195] In the presence of oxidized aluminum islands on Fe(110), iron restructures when heated in water vapor or in oxygen. A much more active catalyst is thereby produced, which carries out ammonia synthesis at rates that are similar to those of the most active Fe(111) crystal face. It was found that an iron-aluminate layer ($FeAl_2O_4$) forms which acts as a substrate for the recrystallization and growth of iron particles with (111) crystal faces. Figure 12 shows a schematic model of the alumina induced restructuring of iron.

It has also been observed that sodium can recrystallize iron oxide.[196] Ordered iron oxide films were grown by evaporation of iron onto a Pt(111) crystal face and subsequent oxidation by heating in oxygen. When sodium is deposited on an FeO film and then the film is heated in vacuum, it completely restructures in a manner shown schematically in Fig. 13. Iron oxide dissolves in sodium, then breaks up into many small particles that do not wet the platinum substrate but form separate aggregates of iron oxide enclosed by sodium. Upon removal of sodium by evaporation, the iron oxide film can be recovered with its original composition and structure.

D. Adsorbate induced reshaping of clusters

Often small metal atom clusters are used for catalysis and for studies in the vapor phase.[197] These clusters may have many different structural shapes that are thermodynamically very similar in energy. Their shapes are therefore sensitive to adsorbates on their surface. A theoretical discussion of this effect has been published.[198]

This is the likely explanation for the unique reactivity that occurs at certain cluster sizes (with "magical numbers" of atoms), and for the abrupt changes of electrical properties such as ionization potential or work function upon adsorption on clusters of certain sizes.[199]

When rhodium particles are heated in hydrogen at elevated temperatures, electron microscopy shows that they sinter and grow (Fig. 14). Upon reaction with oxygen the chemisorption causes a drastic modification of shape as the particles flatten. Upon heating at lower temperature in hydrogen, the flattened platinum particles break up into small clusters and form metal particles of higher dispersion. Finally, upon reheating in hydrogen at high temperature they sinter again to form bigger clusters.[200] This sequence can be repeated many times. It

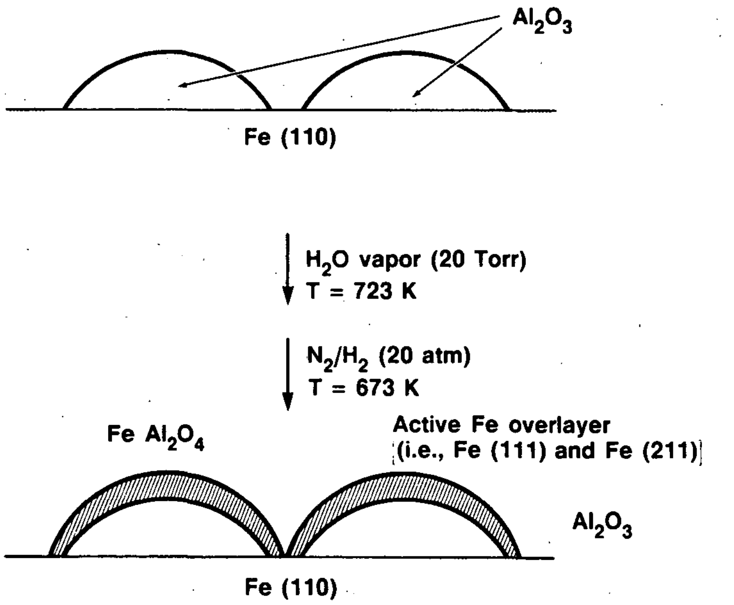

Fig. 12. Alumina induced restructuring of Fe

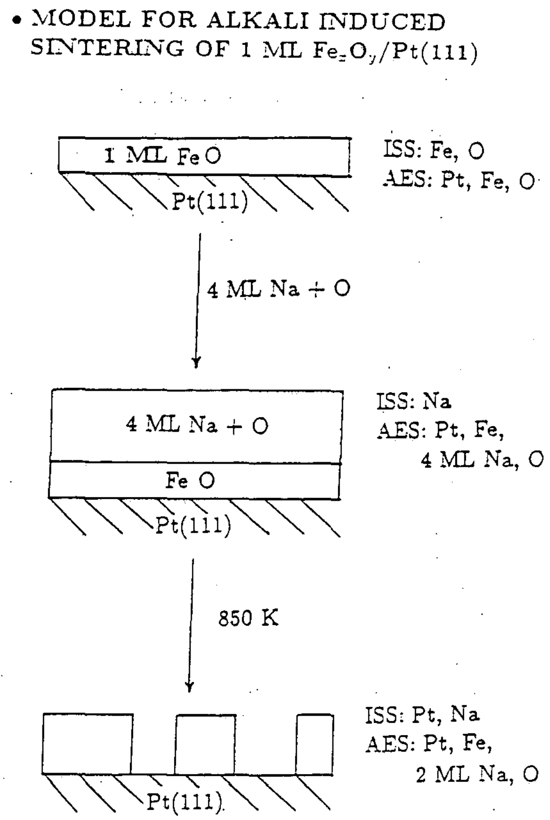

Fig. 13. Restructuring of FeO film by Na

mimics changes in catalyst particle size and dispersion during catalytic reaction, sintering and regeneration. Other adsorbates also induce changes in particle shapes.[201]

Further examples are described in recent reviews.[202,203]

6. Causes and Effects of Adsorbate Induced Restructuring

A. Mechanisms of restructuring

Restructuring in general is the result of optimizing the surface chemical bond. However, different detailed mechanisms are responsible for the variety of restructuring that is observed. In the case of clean surfaces, restructuring can be due to the following causes.

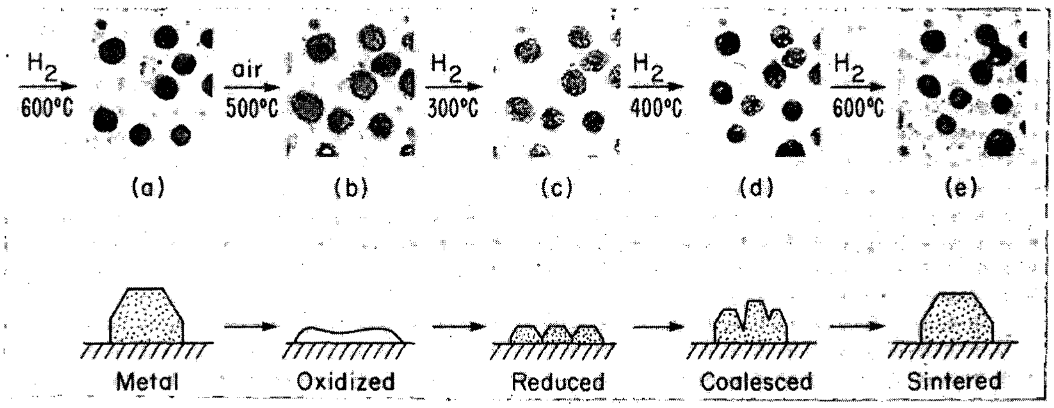

Fig. 14. Changes in rhodium particle morphology with various treatments.

a) Bond shortening: Surface atoms that have lost near neighbors due to the surface formation, have shorter bond lengths to the remaining near neighbors, as formalized in Pauling's bond order/bond length relationship. As a result, interlayer spacings shrink, yielding multilayer relaxations on open metal surfaces such as fcc(110), while surface layers may contract into a different lattice, as in the hexagonal reconstruction of fcc(100).

b) Jahn-Teller-like pairing: In certain cases, such as with Mo(100) and W(100), a clean metal surface with half-filled d-bands has a high density of states near the Fermi level. Then the total energy can be reduced by splitting this density of states by superlattice formation. This can be accomplished by a rebonding arrangement in which zigzag rows of atoms are formed, as happens with bcc(100) surfaces.

c) Rehybridization: The absence of near-neighbor atoms can give rise to substantial rehybridization of orbitals around surface atoms, in particular at semiconductor surfaces. Then different bond angles and bond lengths become favored, often yielding radically different bonding configurations. This applies to most semiconductor surfaces, including the large bond angle distortions on (110) surfaces of III-V compounds,[204] and missing atoms on (111) surfaces of the same compounds.[205]

d) Small facet formation: Since close-packed crystallographic faces have lower surface energy, one can expect such facets to form on more open surfaces. This occurs with the missing-row reconstruction of fcc(110), where small (111) facets are formed. Not resolved is the question why those facets do not systematically grow larger and larger with time.

e) Reduction of the number of dangling bonds: Solids with strong orientational preference in their bonding have difficulty reconciling that preference with a surface. The dangling bonds formed there by removal of atoms to form the surface can to some extent be compensated by new bonding geometries different from those in the bulk. This mechanism overlaps to a large degree with the rehybridization described above. The removal of dangling bonds operates in many elemental semiconductor surfaces, including especially Si(100)–(2x1) and Si(111)–(7x7).

f) Bunching up of steps, leading to facetting: The "equilibrium crystal shape," which describes the optimum external shape of a single crystal, can exhibit sharp corners. These correspond to unstable crystal planes. If a surface is prepared with such an unstable crystal plane, the surface will break up into an alternation of the two nearest stable crystal planes on either side of the unstable plane. This, in the case of Si surfaces cut 5-10° from the (111) face, leads to the formation by diffusion, parallel to the surface, of large step-free (111) terraces, separated by large high-step-density regions.[19]

g) Thermal roughening by disordering of steps: Above a certain temperature, the diffusion of atoms along a stepped surface is rapid enough to cause the steps to lose their linearity. The steps will assume an increasingly curved shape, which lengthens them, so that a larger fraction of the surface atoms is at or near steps. This leads to roughening of the surface also in the direction perpendicular to the surface, as observed in particular on stepped metal surfaces.

An adsorbate can induce or hinder clean-surface restructuring by changing the relative importance of the various restructuring mechanisms. It can thus induce a different restructuring by giving precedence to a different mechanism. An adsorbate can also be responsible for new mechanisms of restructuring. Restructuring mechanisms acting in the presence of adsorbates include the following.

a) Local distortions due to the adsorbate-substrate bond: Distortions of the substrate may occur that improve the coordination number, adsorbate-substrate bond lengths and bond angles relative to the undistorted structure. Many examples of this mechanism are known for adatoms on metal surfaces.

b) Adsorbate preference for certain sites, attainable only through facetting or recrystallization: If an adsorbate requires, for example, a certain coordination number for bonding to a substrate, and if no suitable sites are available on a given substrate, then the substrate may restructure in such a way as to provide the correct type of site.

c) Strong adsorbate-substrate bonds leading to compound formation or to modified surface composition of an alloy: When adsorbate-substrate bonds are much stronger than adsorbate-adsorbate or substrate-substrate bonds, the surface atoms will rearrange in order to maximize the number of adsorbate-substrate bonds.

B. Time scales of adsorbate induced restructuring

The time scales over which surface restructuring occurs vary widely, from an atomic vibration period to beyond the human lifetime. Two main steps in a restructuring process need to be distinguished.

A first and essential step in all adsorbate-induced restructuring is the adsorption itself. If a barrier to adsorption exists, it may slow down the process or prevent it altogether. This happens frequently with adsorption from the gas phase, if the gas molecule has to be decomposed before adsorption. The time scale is then determined by the activation energy to dissociation.

Secondly, the restructuring itself takes time. At a minimum, times on the order of atomic vibration periods are required, if only small relaxations are involved. For more complex restructuring, an activation barrier to formation of the new structure may exist, which may govern the overall rate of the restructuring. This would happen when a chemical reaction must take place, or when a structural phase transition occurs. In the cases that require atomic diffusion, whether perpendicular or parallel to the surface, the diffusion barriers often dominate the overall rate.

In catalytic reactions, slow surface restructuring processes are often detected by the occurrence of long induction periods before steady-state catalytic rates are reached. The induction periods depend on pressure, temperature and particle size of catalysts. This is perhaps the most difficult and complex regime of the adsorbate-induced reconstruction phenomenon. It includes such processes as the build-up of stable hydrocarbon overlayers on metal surfaces, and the formation of carbides, nitrides or oxides by slow solid-state reactions. Nevertheless, it is also one of the most important areas for developing an understanding of ways to fabricate stable catalysts and surface reaction systems.

C. The effect of adsorbate induced restructuring on the nature of active sites

Frequently, one invokes the presence of active sites for crucial, rate-determining bond breaking or bond rearrangements in heterogeneous catalytic reactions. Certain unique site structures are held responsible for important catalytic events. Examples include the dissociation of dinitrogen by the C_7 (7-fold coordinated) sites of Fe(111) or (211) crystal orientations,[195] and the preferential dissociation of C-H bonds at step sites.[206]

Since chemisorbed atoms and molecules may change the positions of metal atoms at or near the surface, it is likely that many of these active sites are only produced upon adsorption and do not exist on clean surfaces. Thus, caution has to be exercised in studies of the surface structure for the purpose of detecting active sites when the surface is clean, since the active sites may not exist on such surfaces. The surface structure should be analyzed in the presence of reactants, reaction intermediates or products to identify the surface structural changes that may occur. These changes may then be correlated with the adsorbate-induced formation of active surface sites as well as the structure of the clean surface.

D. Reconstruction controlled reactions

In certain favorable circumstances surface reconstruction can control the turnover rate of catalyzed surface reactions. This can occur when the reconstruction is an intermediate step in the reaction process.

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D. Reconstruction controlled reactions

In certain favorable circumstances surface reconstruction can control the turnover rate of catalyzed surface reactions. This can occur when the reconstruction is an intermediate step in the reaction process.

There are several examples of surface structural transformations that are intimately coupled with chemical reactions and give rise to oscillatory reaction phenomena. One of these is the oxidation of CO to CO_2 on the platinum (100) face at low pressure.[207,208] Adsorbed CO removes the hexagonal reconstruction of the bare surface to form an unreconstructed metal surface. Oxygen chemisorbs at defect sites on this surface and reacts rapidly with adsorbed CO to desorb as CO_2. This removes CO from the surface and leaves patches of bare metal which reconstruct to the hexagonal phase by an activated process. Oxygen has a very low sticking probability on the clean surface and CO oxidation rates are therefore small. Then new CO adsorbs on the bare patches, removing their reconstruction and repeating the whole process. As a result, the surface oscillates between the two structural forms and this gives rise to the observed temperature and reaction rate fluctuations.

On a different face, (110), of the same metal, Pt, the same reaction also has an oscillatory behavior: in this case the missing-row reconstruction of Pt(110)-(1x2) is implicated.[209] Under certain conditions this reaction even becomes "chaotic," i.e. the oscillator is not simply periodic.[210]

Another reaction on Pt(100) that exhibits oscillatory behavior involving surface reconstruction is that between NO and CO.[211] However, not all oscillatory reactions are driven by the same adsorbate-induced restructuring mechanism. Oscillations on Pt(111), which does not reconstruct, have been attributed to a cyclic oxidation and reduction of the surface.[208]

E. Structure insensitive reactions

A number of chemical reactions occurring at solid surfaces have been found to be surface-insensitive.[212] No matter which crystal face is used, a given reaction maintains the same rate and selectivity. We suggest that adsorbate-induced restructuring can offer a possible mechanism for such behavior. The reaction would simply induce rapid surface restructuring to one particular structure upon adsorption, regardless of the orientation of the initial clean surface. The reaction would then always occur on that restructured surface.

F. Bond breaking of adsorbates induced by surface restructuring

Up to now we have focussed on the influence of adsorbed molecules on the substrate, causing restructuring of surfaces. We now address the reverse process whereby surface restructuring in turn affects the adsorbate itself.

There is ever-increasing evidence that the local restructuring of surface atoms, in the proximity of adsorbing molecules, is the cause of bond breaking in the adsorbates. The relocation of the surface atoms, either parallel or perpendicular to the surface, under the influence of chemisorption changes the local electronic structure, in particular its symmetry properties: this can cause particularly strong interaction with the molecular orbitals of the adsorbates.

This view of reactivity induced by surface restructuring explains most of the properties of the surface chemical bonds. These include the increased reactivity of more open, high-Miller-index and stepped surfaces, and the thermal activation of bond breaking in a narrow temperature range. The more open surfaces undergo restructuring more readily and are known to be more reactive for adsorbate bond breaking. For instance, the more open (111) and (211) crystal faces of iron break the N_2 bonds more readily than the close-packed Fe(110) crystal face.[195] Stepped surfaces of Pt or Ni break H-H, C-H and C-C bonds more easily than the flat (111) crystal face.

It is also commonly observed that C-H, C-C and N-N bonds break in a narrow temperature range on metal surfaces. Such observations are indicative of a concerted reaction that may be induced by a phase change such as a surface restructuring process.

This surface restructuring model of surface reactivity awaits experimental verification using techniques that can probe the surface structure under reaction conditions.

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